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2D and layered materials: from metallorganic frameworks to transition metal dichalcogenides

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PHD THESIS IN PHYSICS

2D and layered materials: from metallorganic frameworks to transition metal dichalcogenides

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Abstract

Research in two-dimensional (2D) and layered materials has emerged as a pivotal frontier in materials science and nanotechnology, holding immense promise for advancing a multitude of technological applications. These materials, characterized by their atomically thin nature and peculiar electronic, optical, and mechanical properties, have opened up new avenues for innovation in fields such as electronics, energy storage, photonics, and beyond. As we delve deeper into the exploration of these materials, we uncover opportunities to engineer novel devices, enhance energy efficiency, and push the boundaries of fundamental scientific understanding.

In this thesis we analyse three inherently two-dimensional systems. On one hand, the focus is on the identification of new systems for heterogeneous catalysis, and on the other hand, the investigation of temperature-driven phase transitions in a prototypical layered material. These systems are investigated through a combination of first-principles and machine learning computational methods, and the results are compared with various experimental findings.

The first part is dedicated to a self-assembled Cobalt Tetra-Pyridyl-Porphirins (CoTPyP) layer on graphene/iridium(111). In this context, akin to many biological molecules, a metal atom is encapsulated within a well-defined chemical environment. This metallic center acts as a single-atom catalyst for heterogeneous catalysis. The addition of further Co atoms, that occupy intermolecular sites, leads to a surprisingly drastic rearrangement of CoTPyPs on the surface with the formation of a 2D metal-organic framework. The structural and electronic properties of these systems are presented, shedding light on the mechanisms underlying the self-assembly process and the substantial structural changes that occur. Particular attention is given to the two inequivalent (intra and intermolecular) Co metal centers, highlighting their inherent differences which result in a different chemical reactivity. This reactivity is explored by showcasing the capacity of the most active site, nestled within the molecule core, to facilitate the formation and stabilization of the OOH-H₂O complex. Additionally, the adsorption of CO on both Co species will be discussed.

Secondly, our attention is directed towards the investigation of transition metal dichalcogenides (TMDs), a diverse class of layered inorganic materials that, under ambient conditions, exhibit a variety of polytypic structures. In many cases, these structures are stabilized by periodic lattice distortions (PLD),

resulting in the formation of charge density waves (CDWs). In this context, we focus on the phase transitions occurring at different temperatures in two specific TMDs: vanadium ditelluride (VTe_2) and tungsten ditelluride (WTe_2).

VTe_2 , in its layered bulk form, assumes a normal 1T phase at high temperatures. However, upon cooling, it undergoes a phase transition to a CDW phase 1T'' at around 475 K. A combination of DFT phonon calculations and pump-and-probe experiments is employed to demonstrate the presence of two phonon modes coupled to the CDW phase. Furthermore, the profound modifications induced in the electronic band structure during this phase transition is illustrated.

As an initial step towards a more comprehensive, temperature-dependent exploration of phase transitions in TMDs, we consider a WTe_2 monolayer, which is stable at room temperature in the 1T' phase. A first-principle interatomic potential suitable for classical molecular dynamics simulations has been developed. Its accuracy is validated through comparisons with phonon calculations performed using fine displacement methods and ab-initio approaches.

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List of Acronyms

AE All-Electron

AIMD Ab Initio Molecular Dynamics

BOMD Born-Oppenheimer Molecular Dynamics

BZ Brillouin Zone

CDW Charge Density Wave

CLS Core Level Shift

CO Carbon Monoxide

Co Cobalt

CoTPyP Cobalt tetra-pyridyl porphirin

DFPT Density Functional Perturbation Theory

DFT Density Functional Theory

DNN Deep Neural Network

DoS Density of States

EP Electrostatic Potential

FeTPP Fe(II)-tetra phenyl porphyrin

GGA Generalized Gradient Approximation

GNN Graph Neural Network

GR Graphene

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H₂O₂ Hydrogen Peroxide

HCH Half Core Hole

HOMO Highest Occupied Molecular Orbital

IFC Interatomic Force Constant

ILDoS Integrated Local Density of States

IP Interatomic Potential

IR Infrared

IR-Vis SFG Infrared-Visible Sum Frequency Generation

KS Kohn-Sham

LDA Local Density Approximation

LDoS Local Density of States

LSDA Local Spin Density Approximation

LUMO Lowest Unoccupied Molecular Orbital

MD Molecular Dynamics

ML Machine Learning

MOF Metal-Organic Framework

MPNN Message Passing Neural Network

NAP Near-Ambient Pressure

NAP-XPS Near-Ambient Pressure X-ray Photoelectron Spectroscopy

NCPPs Norm Conserving Pseudopotentials

NEXAFS Near Edge X-ray Absorption Fine Structure

O₂H Hydroperoxyl radical

OER Oxygen Evolution Reaction

ORR Oxygen Reduction Reaction

OS Oxidation State

PAW Projector Augmented Wave

PBC Periodic Boundary Conditions

PBE Perdew-Burke-Ernzerhof

PDoS Projected Density of States

PES Potential Energy Surface

PLD Periodic Lattice Distortion

PS Pseudopotential

QE Quantum ESPRESSO

RDG Reduced Density Gradient

SAC Single Atom Catalyst

SCF Self-Consistent Field cycle

SOC Spin-Orbit Coupling

STM Scanning Tunneling Microscopy

STS Scanning Tunneling Spectroscopy

TM Transition Metal

TMDCs Transition Metal Dichalcogenides

TPyP 5,10,15,20-tetra(4-pyridyl)porphyrin

TR-OS Time-Resolved Optical Spectroscopy

UHV Ultra High Vacuum

UPS Ultraviolet Photoelectron Spectroscopy

USPPs Ultra Soft Pseudopotentials

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VTe₂ Vanadium Ditelluride

WF Work Function

WTe₂ Tungsten Ditelluride

XPS X-ray Photoelectron Spectroscopy

Introduction

The study presented in this thesis primarily focuses on inherently two-dimensional materials, which represent a rapidly expanding family of systems that have gained increasing attention in recent years. These materials exhibit unique properties due to their reduced dimensionality, in general distinct from their three-dimensional counterparts. Furthermore, they encompass a wide class with varying chemical and physical properties, offering a wide range of candidates with specific attributes of interest. These properties can also be readily controlled through techniques like doping, straining, or charge transfer. As a result, these materials have found applications in diverse fields, including catalysis, energy storage, sensors, electronics, and optoelectronics.

Within this realm, two main classes can be identified: purely two-dimensional materials consisting of a single layer, typically one to a few atoms thick, with atoms covalently bonded to each other, and materials composed of multiple layers bound together by van der Waals interactions.

This thesis will explore both of these major classes. It will delve into the study of self-assembled molecular monolayers on metallic surfaces, with a particular focus on their applications in heterogeneous catalysis. Additionally, an initial investigation of the temperature-driven phase transitions in layered materials is carried on.

The geometrical and electronic characterizations in this study primarily relied on first-principles quantum mechanical simulations based on Density Functional Theory (DFT). The first part of the thesis will describe in detail the computational methods used, while the second part will present the main results. Detailed computational procedures will be reported in the appendix section.

The first set of results will be dedicated to the study of self-assembled Cobalt Tetra-Pyridyl-Porphyrins (CoTPyP) on surfaces. These molecules consist of a single Co atom encapsulated within a well-defined chemical environment provided

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by a porphyrinic macrocycle. This system mimics the structure of fundamental biological molecules in which a metal atom is enclosed by organic ligands that stabilize it and tune its chemical properties, such as the heme group in myoglobin and hemoglobin, responsible for oxygen transport in the blood, and chlorophyll, where a magnesium atom plays a crucial role in photosynthesis.

In this context, CoTPyP molecules are studied when deposited as a single layer on a graphene sheet on an Ir(111) surface. This choice of a metallic substrate allows for precise experimental investigations using various surface science techniques, ensuring a well-defined and controlled chemical environment. Indeed, under specific experimental conditions, these molecules can self-assemble into highly ordered structures with well-defined periodicities. The driving forces behind this self-assembly process, along with the role of the substrate and intermolecular interactions, particularly involving the peripheral pyridinic rings, will be discussed. Additionally, it will be shown how these peripheral groups are responsible for binding additional metal atoms (in this case, Co atoms) that can be evaporated onto the system. This leads to the formation of a 2D metal-organic framework with a significantly different periodicity compared to the monometallic case. The resulting bimetallic system exhibits distinct geometrical structures and electronic properties, which will be thoroughly investigated, along with the chemical reactivity of the system. Particular attention will be given to the study of carbon monoxide adsorption and the formation and stabilization of the OOH-H₂O complex.

The second part of the thesis will focus on the study of inorganic Transition Metal Dichalcogenides (TMDCs). This family of layered materials encompasses a variety of polytypic structures, with structural and electronic properties strongly influenced by the number of layers and stacking order. These materials often exhibit periodic lattice distortions at low temperatures, leading to the formation of a Charge Density Wave (CDW). The investigation will be centered on Vanadium Ditelluride (VTe₂), a relatively less explored member of the TMDC family, with a specific focus on its bulk layered form. This material undergoes a phase transition from a normal 1T phase at high temperatures to a CDW phase 1T' at around 475 K. The structural and electronic properties of both phases will be analyzed, and two phonon modes associated with the CDW phase will be identified.

Furthermore, as an initial step towards a more comprehensive, temperature-dependent exploration of phase transitions in TMDCs using Molecular Dy-

namics (MD) simulations, a first-principles interatomic potential suitable for classical MD simulations will be developed. This potential is generated using machine learning techniques and applied to a different TMDC, Tungsten Diteluride (WTe_2), which is stable at room temperature in the $1T'$ phase. WTe_2 will serve as an example for testing a criterion to establish an appropriate cutoff radius for interatomic interactions, a crucial parameter for obtaining a reliable interatomic potential while maintaining computational efficiency.

In the course of this research, the author primarily conducted computational investigations and was involved in a few experimental sessions concerning the study of molecular layers using synchrotron light. Experimental data acquisition and analysis for these systems were primarily performed by the SFG group, led by Prof. Erik Vesselli and based at the TASC Laboratory of IOM-CNR in Trieste. The pump-and-probe measurements on VTe_2 were conducted instead by the T-REX group, led by Dr. Federico Cilento and hosted at Elettra Sincrotrone Trieste.

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Methods

In this chapter are presented the theoretical framework and the computational methods used for electronic calculations reported in this thesis. DFT forms the basis of these calculations; where the many-body Schrödinger equation is reformulated as a functional dependent on electronic density. DFT is known for its efficiency in striking a balance between computational feasibility and accurate descriptions of structural and electronic properties across a wide range of materials. It has become a standard tool in *ab initio* calculations, essential for understanding and predicting properties in condensed matter and molecular systems. However, DFT is still computationally demanding for large systems and is not suitable for studying dynamical processes within long time scales. To address these limitations while maintaining the accuracy of DFT, a combination of DFT and machine learning techniques is employed.

This chapter is organized into three parts. The first part introduces the fundamental principles of *ab initio* DFT, focusing on the Kohn-Sham approach. The second part explores post-processing techniques for calculating electronic properties useful to compare with experimental measurements. The third part then introduces the basic concepts of machine learning techniques relevant for applications in condensed matter systems.

1.1 DENSITY FUNCTIONAL THEORY CALCULATIONS

1.1.1 SCHRÖDINGER'S EQUATION AND BORN-OPPENHEIMER APPROXIMATION

At a fundamental level, any system of interest in matter physics, whether it involves single atoms, molecules, clusters, or solids, can be described as an ensemble of electrons and nuclei interacting according to the laws of quantum mechanics. Therefore, in principle, every property of the system can be computed by solving the many-body Schrödinger's equation without the need for additional empirical parameters, except for the charge and mass of electrons and nuclei.

In this context, the Schrödinger's equation for a system composed of N electrons and M nuclei can be expressed as:

$$[T_I + T_e + V_{Ie} + V_{ee} + V_{II}]\Phi(\{\mathbf{R}_I\}, \{\mathbf{r}_j\}) = E \Phi(\{\mathbf{R}_I\}, \{\mathbf{r}_j\}) \quad (1.1)$$

where T_I and T_e are the ionic and electronic kinetic energies, whereas V_{ee} , V_{Ie} , and V_{II} are the electron-electron, electron-ion, and ion-ion potential energies operators, and read:

$$\begin{aligned} T_I &= - \sum_{I=1}^M \frac{\hbar^2}{2M_I} \nabla_I^2 \\ T_e &= - \sum_{j=1}^N \frac{\hbar^2}{2m_e} \nabla_j^2 \\ V_{Ie} &= - \sum_{I=1}^M \sum_{j=1}^N \frac{Z_I e^2}{|\mathbf{R}_I - \mathbf{r}_j|} \\ V_{ee} &= \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ V_{II} &= \frac{1}{2} \sum_{\substack{I,J=1 \\ I \neq J}}^M \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} \end{aligned} \quad (1.2)$$

$\Phi(\{\mathbf{R}_I\}, \{\mathbf{r}_j\})$ in eq. (1.1) is the many-body wavefunction, where $\{\mathbf{R}_I\}$ ($I =$

$1, \dots, M$) and $\{\mathbf{r}_j\}$ ($j = 1, \dots, N$) are the sets of the ionic and electronic spatial coordinates.

In practice, this highly complex problem is impossible to tackle both analytically and numerically, and it necessitates the use of approximations. The most fundamental of these approximations is the *Born-Oppenheimer approximation* [1]. It is based on the large difference between the masses of nuclei and electrons which allows to decouple the dynamics of the fast degrees of freedom (the electrons) from the dynamics of the slow variables (the nuclei). In a first stage the nuclei can be regarded as fixed in selected spatial configurations, and attention is focused on the so called potential energy surfaces $E(\{\mathbf{R}_I\})$ which specify the electronic energies E as a function of the chosen nuclear positions $\{\mathbf{R}_I\}$. Then the dynamics of the nuclear degrees of freedom is determined by the nuclear kinetic energy and by the effective potential energies $E(\{\mathbf{R}_I\})$. Formally this amounts to write the total wavefunction as a product of an electronic and a nuclear wavefunction:

$$\Phi(\{\mathbf{R}_I\}, \{\mathbf{r}_j\}) = \psi(\{\mathbf{r}_j\}; \{\mathbf{R}_I\}) \phi(\{\mathbf{R}_I\}) \quad (1.3)$$

where $\phi(\{\mathbf{R}_I\})$ is the solution of the nuclear equation

$$[T_I + E(\{\mathbf{R}_I\})] \phi(\{\mathbf{R}_I\}) = \epsilon \phi(\{\mathbf{R}_I\}) \quad (1.4)$$

and $\psi(\{\mathbf{r}_j\}; \{\mathbf{R}_I\})$ satisfies the Schrödinger equation for the electrons in the external potential of the nuclei kept fixed in the configuration $\{\mathbf{R}_I\}$:

$$[T_e + V_{Ie} + V_{ee}] \psi(\{\mathbf{r}_j\}; \{\mathbf{R}_I\}) = E(\{\mathbf{R}_I\}) \psi(\{\mathbf{r}_j\}; \{\mathbf{R}_I\}) \quad (1.5)$$

1.1.2 HÖHENBERG-KOHN THEOREMS AND KOHN-SHAM EQUATIONS

Although the Born-Oppenheimer approximation greatly simplifies the original problem, eq. (1.5) remains challenging due to the interactions among the electrons themselves. Notably, the electronic wavefunction $\psi(\mathbf{r}_j)$ ¹ cannot be expressed as a product of single-particle wavefunctions. Furthermore, $\psi(\mathbf{r}_j)$ even for spinless particles has $3N$ variables, resulting in a large number of degrees of

¹Hereafter, nuclei will be considered fixed, and for the sake of notation simplicity, their coordinates will be omitted.

1.1. DENSITY FUNCTIONAL THEORY CALCULATIONS

freedom even for small systems.

However, in 1964 Hönenberg and Kohn formulate two theorems demonstrating that any property of a many electron system can be viewed as a functional of the ground state electronic density alone and that a system of interacting electrons can be described by a set of non-interacting electrons moving in an effective potential [2].

Starting from the Schrödinger equation for the electrons, in eq. (1.5), the total energy can be given as the expectation value on the wavefunction $\psi = \psi(\{\mathbf{r}\})$:

$$E = \langle \psi | T_e + V_{ee} | \psi \rangle + \int v_{ext}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \quad (1.6)$$

where

$$v_{ext}(\mathbf{r}) = - \sum_{I=1}^M \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R}_I|} \quad (1.7)$$

and $n(\mathbf{r})$ is the electronic density:

$$n(\mathbf{r}) = N \int |\psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \cdots d\mathbf{r}_N \quad (1.8)$$

The first theorem states that $v_{ext}(\mathbf{r})$ is, up to a constant, a unique functional of the electronic density $n(\mathbf{r})$. Since $v_{ext}(\mathbf{r})$ fixes the Hamiltonian, it follows that the total energy itself is a unique functional of the electronic density $n(\mathbf{r})$, and it can be written as:

$$E[n(\mathbf{r})] = F[n(\mathbf{r})] + \int n(\mathbf{r}) v_{ext}(\mathbf{r}) d\mathbf{r} \quad (1.9)$$

where $F[n(\mathbf{r})]$ is the universal functional of the electronic density corresponding to the expectation value of $T_e + V_{ee}$ valid for any external potential and number of particles, while v_{ext} is a system dependent term.

The second theorem states that, when the potential v_{ext} is given, the total energy has a minimum at the ground state electronic density $n_0(\mathbf{r})$

$$E[n_0(\mathbf{r})] = \min_{n(\mathbf{r})} E[n(\mathbf{r})] = F[n_0(\mathbf{r})] + \int n_0(\mathbf{r}) v_{ext}(\mathbf{r}) d\mathbf{r}. \quad (1.10)$$

However, the universal functional $F[n(\mathbf{r})]$ for a system of interacting electrons is not known. Therefore, in order to obtain the ground state energy, a further approximation is needed.

The central concept in the Kohn-Sham (KS) approach is to replace the complex interacting many-body system of electrons with an auxiliary system that is computationally more tractable. The KS method assumes that the ground state density of the original interacting system is equivalent to that of a non-interacting system of electrons, which move in an effective potential $v_{KS}(\mathbf{r})$. Under this assumption, the Hohenberg-Kohn theorem remains valid, and the unique functional $F[n(\mathbf{r})]$ corresponds to the kinetic energy of non-interacting electrons, denoted as $T_0[n(\mathbf{r})]$. The density functional $F[n(\mathbf{r})]$ for the interacting system can then be expressed as the sum of the kinetic energy of a non-interacting electron gas with the same density $n(\mathbf{r})$ as the real system and additional terms that describe the interparticle interaction:

$$F[n(\mathbf{r})] = T_0[n(\mathbf{r})] + \frac{e^2}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[n(\mathbf{r})]. \quad (1.11)$$

The second term on the right-hand side of eq. (1.11) represents the classical Coulomb interaction among the electrons, described through their charge density, and is commonly known as the Hartree term. On the other hand, $E_{xc}[n(\mathbf{r})]$ represents the exchange-correlation energy, which accounts for all the many-body effects that are not described by the other terms. In practice, this term encompasses all the differences between the non-interacting fictitious system and the real interacting one, including corrections for the electron-electron interaction and the kinetic energy. Therefore, this term serves as a container for our lack of knowledge about $F[n(\mathbf{r})]$.

This formulation is particularly valuable when the functional $F[n(\mathbf{r})]$ is minimized under the constraint of conserving the total number of particles N to obtain the ground state physical properties of the real system. In fact, from eq. (1.11), it is relatively straightforward to derive the effective potential v_{KS} that acts on the electrons of the fictitious non-interacting system. If the total energy functional $E^0[n(\mathbf{r})]$ for the non-interacting electron gas

$$E^0[n(\mathbf{r})] = T_0[n(\mathbf{r})] + \int v_{KS}(\mathbf{r})n(\mathbf{r})d\mathbf{r} - \mu \left(\int n(\mathbf{r})d\mathbf{r} - N \right) \quad (1.12)$$

is imposed to be minimized by the same electron density $n_0(\mathbf{r})$ which also

1.1. DENSITY FUNCTIONAL THEORY CALCULATIONS

minimizes the total energy of the interacting system

$$E[n(\mathbf{r})] = T_0[n(\mathbf{r})] + \int v_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \frac{e^2}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[n(\mathbf{r})] - \mu' \left(\int n(\mathbf{r})d\mathbf{r} - N \right) \quad (1.13)$$

the expression for the effective KS potential is given by:

$$v_{KS}(\mathbf{r}) = v_{ext}(\mathbf{r}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}) \quad (1.14)$$

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \quad (1.15)$$

where the chemical potentials μ and μ' are the Lagrange multipliers that guarantee the conservation of the total number of particles N in the interacting and non-interacting systems, respectively. Therefore, V_{KS} is defined up to a constant difference between μ and μ' .

The resulting effective Hamiltonian for the system describes a non-interacting electron gas experiencing the effective potential V_{KS} , which encompasses all the interparticle interactions present in the real system. The electronic problem can, therefore, be tackled using fictitious one-particle wavefunctions, enabling the charge density to be expressed as:

$$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2 \quad (1.16)$$

where i is an index that runs over all the single particle states, and f_i is the occupation number of the state i .

By minimizing the energy functional for non-interacting electrons with respect to ψ_i in the constraint of a fixed number of electrons, a set of Schrödinger-like equations can be derived, commonly known as the Kohn-Sham equations:

$$\hat{H}_{KS}\psi_i(\mathbf{r}) = \left[-\frac{\hbar^2}{2m_e} \nabla^2 + v_{KS}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}). \quad (1.17)$$

It is important to emphasize that the KS wavefunctions do not possess a direct physical interpretation. They represent the eigenstates of a fictitious one-body density matrix and cannot be regarded as the wavefunctions for the electrons

of the real system. Instead, they serve as electronic orbitals for the auxiliary non-interacting electron gas.

Additionally, the set of KS equations is highly nonlinear due to the interdependence of the effective potential v_{KS} on the charge density $n(\mathbf{r})$, which itself relies on the KS orbitals $\psi_i(\mathbf{r})$. Nevertheless, this nonlinearity implies that an iterative approach can be employed to solve the system. Starting with an initial guess for the wavefunctions and potential, both quantities evolve iteratively until self-consistency is reached. Hence, solving iteratively the KS equations is equivalent to minimizing the total energy functional for the N-electron system. Using a set of orthonormal single-particle wavefunctions, the ground state total energy can also be expressed as:

$$E_0 = \sum_i f_i \epsilon_i - \frac{e^2}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[n(\mathbf{r})] - \int v_{xc}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_{ion}. \quad (1.18)$$

Here, the Hartree and exchange-correlation contributions serve to address the double counting and miscounting of the same quantities in the sum of the eigenvalues, respectively. The final term, E_{ion} , is an energy term that considers the direct Coulomb interactions among the ionic cores.

The theoretical approach described so far is expected to be very efficient when the dominant part of the energy consists of the kinetic and electrostatic terms because they are described without any approximation. However, the success in studying real materials depends very strongly on how the (hopefully small) exchange-correlation contribution is described. In fact, the exchange-correlation energy is the only term that cannot be computed exactly, and it is the most challenging part of the DFT problem. Therefore, the accuracy of the DFT results depends on the quality of the approximations used to describe the exchange-correlation energy.

1.1.3 EXCHANGE-CORRELATION FUNCTIONALS

The simplest approximation for the exchange-correlation energy, $E_{xc}[n(\mathbf{r})]$, is given by the Local Density Approximation (LDA) [3]. In this approximation, each small volume of the system behaves as a homogeneous electron gas with a

1.1. DENSITY FUNCTIONAL THEORY CALCULATIONS

density equal to the local density of the inhomogeneous system:

$$E_{xc}^{LDA}[n(\mathbf{r})] = \int \epsilon_{xc}^{hom}(n(\mathbf{r})) n(\mathbf{r}) d\mathbf{r} \quad (1.19)$$

where $\epsilon_{xc}^{hom}(n(\mathbf{r}))$ is the exchange-correlation energy per electron of a homogeneous electron gas with density $n(\mathbf{r})$. The exchange-correlation potential is obtained as a functional derivative of eq. (1.19):

$$v_{xc}^{LDA}(\mathbf{r}) = \frac{\delta E_{xc}^{LDA}[n(\mathbf{r})]}{\delta n(\mathbf{r})} = \epsilon_{xc}^{hom}(n(\mathbf{r})) + n(\mathbf{r}) \frac{\delta \epsilon_{xc}^{hom}(n(\mathbf{r}))}{\delta n(\mathbf{r})} \quad (1.20)$$

In order to model magnetic materials, the Local Spin Density Approximation (LSDA) was developed. In this approach, the exchange-correlation energy functional explicitly depends on the two spin populations separately:

$$E_{xc}^{LSDA}[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})] = \int \epsilon_{xc}^{hom}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})) n(\mathbf{r}) d\mathbf{r} \quad (1.21)$$

where

$$v_{xc}^{\sigma}(\mathbf{r}) = \frac{\delta E_{xc}^{LSDA}[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})]}{\delta n_{\sigma}(\mathbf{r})} \quad (1.22)$$

and

$$n_{\sigma}(\mathbf{r}) = \sum_i f_i^{\sigma} |\psi_i^{\sigma}(\mathbf{r})|^2 \quad (1.23)$$

$$n(\mathbf{r}) = \sum_{\sigma} n_{\sigma}(\mathbf{r}) \quad (1.24)$$

The magnetization, denoted as $m(\mathbf{r})$, is determined by:

$$m(\mathbf{r}) = n_{\uparrow}(\mathbf{r}) - n_{\downarrow}(\mathbf{r}) \quad (1.25)$$

LDA and LSDA are particularly efficient in systems with reasonably slowly varying spatial density. However, they tend to overestimate binding energies and underestimate bond lengths.

To address these limitations, corrections to the LDA functional can be applied, specifically in terms of the density gradient, using the so-called Generalized Gradient Approximation (GGA) [4]:

$$E_{xc}^{GGA}[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})] = \int \epsilon_{xc}^{hom}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}), \nabla n_{\uparrow}(\mathbf{r}), \nabla n_{\downarrow}(\mathbf{r})) n(\mathbf{r}) d\mathbf{r} \quad (1.26)$$

Compared to LDA, GGA offers improvements in terms of binding energy and bond length, correcting or sometimes over-correcting the LDA values [5]. Furthermore, GGA enhances the description of inhomogeneous systems, such as transition metals, where LDA is completely inadequate. Several forms of GGA have been proposed, and the most widely used is the Perdew-Burke-Ernzerhof (PBE) [5].

1.1.4 PLANE WAVES BASIS SET

To make practical use of DFT, the complex integro-differential KS equations need to be transformed into an algebraic form suitable for numerical solutions. In the case of periodically repeating crystalline solids, where the Bloch theorem is applicable, it is possible to expand the electronic wavefunctions and operators in the Hamiltonian using a plane wave basis set.

According to the Bloch theorem, the single-particle electronic wavefunctions in a periodic potential, represented by $V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r})$, can be expressed in momentum space as a plane wave modulated by a periodic function $u_{n,\mathbf{k}}(\mathbf{r})$, which shares the periodicity of the lattice, $u_{n,\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n,\mathbf{k}}(\mathbf{r})$:

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n,\mathbf{k}}(\mathbf{r}), \quad (1.27)$$

where n represents the band index, and $\mathbf{k}$ denotes the crystal momentum of the electron, which is defined within the first Brillouin Zone (BZ) of the reciprocal space. The periodic part of this expression is expanded using a plane wave basis set:

$$u_{n,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} c_{n,\mathbf{k}+\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}, \quad (1.28)$$

where Ω is the volume of the cell, $\mathbf{G}$ is a reciprocal lattice vector, and $c_{n,\mathbf{k}+\mathbf{G}}$ are the coefficients of the plane waves. Therefore, the KS orbitals (eq. (1.27)) can be expressed in terms of the plane wave basis set as follows:

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} c_{n,\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}. \quad (1.29)$$

This expansion is exact in the limit of an infinite plane wave basis set. In practical calculations, the summation is truncated to include only the $\mathbf{G}$ -vectors that have

1.1. DENSITY FUNCTIONAL THEORY CALCULATIONS

a kinetic energy lower than a cutoff energy E_{cut} :

$$\frac{\hbar^2}{2m_e}|\mathbf{k} + \mathbf{G}|^2 \leq E_{cut}. \quad (1.30)$$

The accuracy of this approximation must be verified by convergence tests of the quantities of interest as a function of E_{cut} . The ground-state density can also be expanded in plane waves:

$$n(\mathbf{r}) = \sum_{\mathbf{G}} n(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}}, \quad (1.31)$$

where $n(\mathbf{G})$ is the charge density in the reciprocal space. The coefficients $n(\mathbf{G})$ are given by:

$$n(\mathbf{G}) = \frac{1}{\Omega} \sum_n \int_{BZ} f_{n,\mathbf{k}} \sum_{\mathbf{G}'} c_{n,\mathbf{k}+(\mathbf{G}'-\mathbf{G})}^* c_{n,\mathbf{k}+\mathbf{G}'} d\mathbf{k}. \quad (1.32)$$

The modulus of the largest $\mathbf{G}$ -vector appearing in eq. (1.31) is twice as large as the maximum $\mathbf{G}$ -vector determined by the cutoff energy in eq. (1.30) because it depends on the vector difference between $\mathbf{k} + \mathbf{G}$ and $\mathbf{k} + \mathbf{G}'$. As a consequence, the kinetic energy cutoff of the charge density is four times larger than the kinetic energy cutoff of the wavefunction.

Moreover, the integral over the BZ appearing in eq. (1.32) is replaced, in numerical calculations, with a summation over a discrete grid of $\mathbf{k}$ -points. One of the most used techniques to sample the BZ is the Monkhorst-Pack grid [6], which is a homogeneous grid with rows and columns of $\mathbf{k}$ -points running parallel to the reciprocal lattice vectors.

By making use of the plane wave expression for the KS orbitals, the KS equation in the reciprocal space becomes a set of equations for the coefficients $c_{n,\mathbf{k}+\mathbf{G}}$:

$$\sum_{\mathbf{G}'} \left[-\frac{\hbar^2}{2m_e}|\mathbf{k} + \mathbf{G}|^2 + v_{KS}(\mathbf{G}, \mathbf{G}') \right] c_{n,\mathbf{k}+\mathbf{G}'} = \epsilon_{n,\mathbf{k}+\mathbf{G}} c_{n,\mathbf{k}+\mathbf{G}}. \quad (1.33)$$

As the original KS equations in eq. (1.17), they can be solved iteratively, and the coefficients are used to compute the charge density. This charge density is then employed to construct a new KS potential, and the equations are solved again until self-consistency is reached. This recursive procedure defines a Self-Consistent Field cycle (SCF).

1.1.5 PSEUDOPOTENTIALS

However, a problematic component of the Kohn-Sham potential in the plane wave representation is the nuclear potential $V_{\text{ext}}(\mathbf{G} + \mathbf{G}')$. Indeed, the Coulomb electron-ion interaction decays too slowly to be accurately represented by a small number of plane waves. A large kinetic energy cutoff is also required to describe the rapid oscillations of the wavefunction of the core electrons. However, the localized core electrons do not significantly contribute to the chemical reactivity of the system, which is mainly led by the valence electrons.

In this picture, the combined effects of the nucleus and the core electrons on the valence electrons through the Coulomb interaction are replaced by an effective potential known as a pseudopotential. These pseudopotentials are necessary to generate smooth and nodeless pseudo-wavefunctions that match the all-electron wavefunctions outside a specified radius and are sufficiently smooth within the core region to be accurately represented by a small number of plane waves.

The requirement that the norm of the wavefunctions must be conserved gives rise to Norm Conserving Pseudopotentials (NCPs) [7]. This condition is essential to ensure the accurate scattering properties around the atomic reference energy, and it yields significantly more precise results compared to empirical pseudopotentials that do not meet this requirement.

A new class of pseudopotentials, called Ultra Soft Pseudopotentials (USPPs), was later introduced by Vanderbilt [8]. These pseudopotentials relax the constraint on the total charge, allowing for the construction of very smooth pseudo-wavefunctions while substantially reducing the number of plane waves needed for the expansion. Importantly, these USPPs do not compromise the atomic scattering properties. Although this approach is technically complex, it speeds up calculations, particularly for elements like nitrogen, oxygen, and fluorine, whose norm-conserving pseudopotentials are still relatively *hard* and require a significant number of Fourier components to be accurately represented.

1.2 ELECTRONIC PROPERTIES' CALCULATION

In this work the DFT calculations were performed using Quantum ESPRESSO (QE) distribution [9, 10, 11]. This suite of codes is equipped with a main executable `pw.x` which performs the self-consistent solution of KS equations, while

1.2. ELECTRONIC PROPERTIES' CALCULATION

on top of that other satellite codes make it possible to perform post-processing tasks. Here are discussed the ones used in this work.

1.2.1 DENSITY OF STATES

The Density of States (DoS) is a function of energy (E) and is defined as:

$$DoS(E) \propto \sum_n \int_{BZ} d\mathbf{k} \delta(\epsilon_{n,\mathbf{k}} - E) \quad (1.34)$$

where $\epsilon_{n,\mathbf{k}}$ are the eigenvalues of KS equation (eq. (1.33)). To understand the character of the bonds between different atoms or the distribution of the electrons in the system, it is useful to introduce the Projected Density of States (PDoS), which provides the projection of the DoS on the atomic orbitals:

$$PDoS_\alpha(E) \propto \sum_n \int_{BZ} d\mathbf{k} |\langle \Phi_\alpha^{at} | \psi_{n,\mathbf{k}} \rangle|^2 \delta(\epsilon_{n,\mathbf{k}} - E), \quad (1.35)$$

where Φ_α^{at} is the atomic orbital. The subscript α stands for atomic index and quantum numbers.

1.2.2 STM AND STS IMAGES

To compare with experiments, it is useful to compute the Scanning Tunneling Microscopy (STM) and Scanning Tunneling Spectroscopy (STS) images. To compute them, the important quantities are the Local Density of States (LDoS):

$$LDoS(\mathbf{r}, E) = \sum_n \int_{BZ} d\mathbf{k} |\psi_{n,\mathbf{k}}(\mathbf{r})|^2 \delta(\epsilon_{n,\mathbf{k}} - E) \quad (1.36)$$

and the Integrated Local Density of States (ILDoS):

$$ILDoS(\mathbf{r}) = \int_{\epsilon_F}^{\epsilon_F + V_{bias}} LDoS(\mathbf{r}, E) dE. \quad (1.37)$$

Here ϵ_F is the Fermi energy and V_{bias} is the bias voltage experimentally applied between the tip of the microscope and the sample.

In the Tersoff-Hamann approximation [12], where the tip is modeled as a spherical potential well in which only the s-wave solution is considered, it is

possible to demonstrate that the tunneling current I between the tip and the sample is proportional to the ILDoS:

$$I(\mathbf{r}) \propto \text{ILDoS}(\mathbf{r}). \quad (1.38)$$

Therefore, the STM image at constant height can be obtained by plotting the ILDoS at fixed value of the bias voltage V_{bias} and z coordinate. STS images, instead measure the differential conductance (dI/dV), which is approximately proportional to the LDoS:

$$\frac{dI(\mathbf{r})}{dV} \propto \text{LDoS}(\mathbf{r}, E). \quad (1.39)$$

1.2.3 CORE LEVEL SHIFT

To characterize the chemical composition and local atomic bonding at surfaces, one of the most valuable experimental techniques is *core level photoelectron spectroscopy* [13]. The set of binding energies of core electrons serves as a distinctive fingerprint for each atomic element. Measuring these binding energies via photoemission spectra enables the detailed, and in some cases quantitative, determination of the chemical composition of surfaces and thin films. Furthermore, the precise value of the binding energy is highly sensitive to the chemical environment, encompassing alterations in geometry, charge, or neighboring atoms. This Core Level Shift (CLS) can then be used to identify differences in the local and chemical environment of several atoms of the same species in the same sample or changes between different samples.

In computing the CLS from DFT calculations, a final-state approximation is used and the time-dependent perturbation due to incident magnetic field is neglected. Here, the valence electrons are allowed to relax by means of a self-consistent calculation, while the core electrons are kept frozen with a core-hole pseudopotential. The CLS for two atoms i and j of the same specie if computed in the All-Electron (AE) approach is given by:

$$\text{CLS}(j - i) = \Delta \text{BE}(j - i) = \text{BE}^{\text{AE}}(j) - \text{BE}^{\text{AE}}(i) \quad (1.40)$$

with

$$\text{BE}^{\text{AE}}(i) = E_{\text{tot}}^{\text{AE}}(i^*) - E_{\text{tot}}^{\text{AE}}(\text{GS}) \quad (1.41)$$

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where GS and i^* identify the same system configuration in his ground state and with a core hole in atom i , respectively. Since the interest is to compute CLS in the Pseudopotential (PS) approach, quantities computed in that way can be introduced:

$$BE^{AE}(i) \simeq BE^{PS}(i) + \Delta E_{at}^{AE-PS}(i) \quad (1.42)$$

with

$$BE^{PS}(i) = E_{tot}^{PS}(i^*) - E_{tot}^{PS}(GS) \quad (1.43)$$

and

$$\Delta E_{at}^{AE-PS}(i) = E_{at}^{AE}(i^*) - E_{at}^{PS}(i^*) - [E_{at}^{AE}(GS) - E_{at}^{PS}(GS)] \quad (1.44)$$

where E_{at}^{PS} and E_{at}^{AE} are the total energies of the isolated atom in the PS and AE approaches, respectively, computed with a core-hole and in its ground state. Here an approximation was made by considering that the difference between the total energies computed for the isolated atom is the same as the difference between the total energies computed for the same atom in the whole system under study. This is a reasonable approximation since the core-hole is localized and pseudopotential are constructed to reproduce the all-electron valence states. Now, the CLS in the PS approach can be written as:

$$CLS(j-i) = BE^{PS}(j) - BE^{PS}(i) + \Delta E_{at}^{AE-PS}(j) - \Delta E_{at}^{AE-PS}(i) \quad (1.45)$$

but since the last two terms are computed for the same atomic specie, they are equal and cancel out, so that:

$$CLS(j-i) = BE^{PS}(j) - BE^{PS}(i) = E_{tot}^{PS}(j^*) - E_{tot}^{PS}(GS) - [E_{tot}^{PS}(i^*) - E_{tot}^{PS}(GS)] \quad (1.46)$$

and finally:

$$CLS(j-i) = E_{tot}^{PS}(j^*) - E_{tot}^{PS}(i^*) \quad (1.47)$$

This equation states that the CLS between two atoms of the same species can be computed in the pseudopotential approach as the total energy difference between the two systems, each with a core-hole in one of the two atoms, respectively. It then allows to access only the CLS and not the absolute binding energy of the core level.

In pratical applications employing Periodic Boundary Conditions (PBC), the presence of a localized charge, such as the one of a core-hole, can lead to the divergence of electrostatic sums. For this reason it is necessary that the core-

hole PS has an extra valence electron to compensate for the missing core charge. However, in particular for isolated molecules, this approach can lead to wrong results. Hence, a $+1 e^-$ jellium background is used to compensate for the extra valence electron reflecting the experimental emission of the e^- from the sample.

1.2.4 NEXAFS SPECTRA

STM is the most direct technique to investigate molecular adsorption. However, another commonly adopted method is Near Edge X-ray Absorption Fine Structure (NEXAFS), which displays several interesting features. In particular, it is element specific following the specificity of core energies. Furthermore, the intensity of NEXAFS resonances depend on the transition dipole moment of the molecular orbitals. Hence, if the surface overlayer displays a specific orientation, the latter can be inferred from the intensity variation of NEXAFS electronic transitions at different polarization of the incident light. This is a frequently used procedure to quantitatively determine tilting angles.

In the present work we focus on NEXAFS spectra at the N K-edge, since no other nitrogen atoms are present in the system under study except for two inequivalent species in TPyP molecules. In order to distinguish the contribution from these two species, a *building block* approach was used, by comparing with the resonances of Fe(II)-tetra phenyl porphirin (FeTPP) and pyridine molecules, both previously studied in literature, since they present exclusively one of the two N species [14, 15]. In order to confirm this attribution to resonances and explain the dichroic behaviour, NEXAFS spectra were computed by means of DFT calculations.

In this framework, the photon energy adsorbed in a specific transition from the ground state is given by the difference between the energy of the final and initial state:

$$h\nu = E_f - E_i \quad (1.48)$$

Here, introducing the occupation numbers n_i and n_f of the initial and final orbitals, and introducing the quantities $m_i = m_f = 1/2$, the energies can be written as:

$$\begin{aligned} E_i &= E(n_i = 1, n_f = 0) = E(m_i + 1/2, m_f - 1/2) \\ E_f &= E(n_i = 0, n_f = 1) = E(m_i - 1/2, m_f + 1/2) \end{aligned} \quad (1.49)$$

1.2. ELECTRONIC PROPERTIES' CALCULATION

Now we consider Janak's theorem [16] which states that the orbital energy ϵ_i is given by the derivative of the Kohn-Sham energy with respect to the occupation number n_j of the orbital j :

$$\epsilon_j = \frac{\partial E}{\partial n_j} \quad (1.50)$$

Then, following Slater's transition state theory [17], we expand both E_i and E_f in a Taylor series around the transition state $n_i = n_f = 1/2$ up to the second order in the occupation numbers:

$$\begin{aligned} E_i = E(m_i, m_f) &+ \frac{1}{2} \left(\epsilon_f^{(1/2, -1/2)} - \epsilon_i^{(1/2, -1/2)} \right) \\ &+ \frac{1}{2!} \left(\frac{1}{2} \right)^2 \left(\frac{\partial^2 E}{\partial n_i^2} - 2 \frac{\partial^2 E}{\partial n_i \partial n_f} + \frac{\partial^2 E}{\partial n_f^2} \right) \\ &+ \dots \end{aligned} \quad (1.51)$$

$$\begin{aligned} E_f = E(m_i, m_f) &+ \frac{1}{2} \left(\epsilon_f^{(1/2, -1/2)} - \epsilon_i^{(1/2, -1/2)} \right) \\ &- \frac{1}{2!} \left(\frac{1}{2} \right)^2 \left(\frac{\partial^2 E}{\partial n_i^2} - 2 \frac{\partial^2 E}{\partial n_i \partial n_f} + \frac{\partial^2 E}{\partial n_f^2} \right) \\ &+ \dots \end{aligned} \quad (1.52)$$

The superscript (n_i, n_f) indicates the occupations of the initial and final states, respectively. As a consequence, the transition energy up to the second order is given by:

$$h\nu = \epsilon_f^{(1/2, -1/2)} - \epsilon_i^{(1/2, -1/2)} \quad (1.53)$$

Up to now we have considered the constant number of electrons in the system, i.e. $\sum_j n_j = N$. However, in order to construct a complete NEXAFS spectrum using eq. (1.53), it would be required to compute the electronic structure of the system for all the possible final-state orbitals. Accordingly, Triguero and coworkers [18] proposed an approximation to Slater's approach by neglecting the fractional occupation of the final state f :

$$h\nu = \epsilon_f^{(1/2, 0)} - \epsilon_i^{(1/2, 0)} \quad (1.54)$$

Here has to be underlined that the number of electrons is reduced to $N - 1/2$. We can also notice that the last term in eq. (1.54) is the core electron binding energy for the state i , so that if interested in relative energy scale, CLS ΔE_i with

respect to the average core electron binding energy E_i^{avg} should be considered:

$$h\nu = \epsilon_i^{(1/2,0)} + \Delta E_i + E_i^{avg} \quad (1.55)$$

X-ray absorption cross-section is computed using Fermi golden rule:

$$\sigma(\omega) = 4\pi^2 \alpha \hbar \omega \sum_f |\langle \psi_f | D | \psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega) \quad (1.56)$$

Here α is the fine structure constant, $\hbar\omega$ is the photon energy, D is the dipole operator, $|\psi_i\rangle$ and $|\psi_f\rangle$ are the initial and final single particle KS states, respectively.

Dipole operator is given by:

$$D = \hat{\epsilon} \cdot \vec{r} + \frac{i}{2}(\hat{\epsilon} \cdot \vec{r})(\vec{k} \cdot \vec{r}) \quad (1.57)$$

Where $\hat{\epsilon}$ and $\vec{k}$ are the polarization and wave vector of the incident light, respectively and $\vec{r}$ is the electron coordinate.

In the pseudopotential approach, the all-electron wavefunction $|\psi_f\rangle$ needed in eq. (1.56) is obtained from the pseudowave function $|\tilde{\psi}_f\rangle$ by means of Projector Augmented Wave (PAW) method [19].

In `xspectra.x` code of Quantum ESPRESSO distribution the summation over the final states is avoided by using Lanczos recursive algorithm [20].

Finally, to compare with experimental data acquired at normal and grazing incidence, multiple calculations were carried on setting the polarization vector $\hat{\epsilon}$ in eq. (1.57) parallel and perpendicular to the surface, respectively.

In order to take in account CLS of the two inequivalent N species according to eq. (1.55), `molecularnexafs.x` code was used [21, 22].

1.2.5 REDUCED DENSITY GRADIENT

Reduced Density Gradient (RDG) is a useful quantity to characterize the nature of non-covalent interactions [23]. It is defined as:

$$s(\mathbf{r}) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla n(\mathbf{r})|}{n(\mathbf{r})^{4/3}} \quad (1.58)$$

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When a weak inter- or intramolecular interaction is present, there is a crucial change in the reduced gradient between the interacting atoms, producing density critical points between interacting fragments. Troughs appear in $s(\mathbf{r})$ associated with each critical point. Since the behavior of s at low densities is dominated by n , s tends to diverge except in the regions around a density critical point, where ∇n dominates, and s approaches zero.

However, RDG itself can not distinguish between attractive and repulsive interactions. To overcome this limitation the second derivative of the electron density along the main axis of variation is considered. Indeed the sign of $\nabla^2 n$ indicates whether the density is concentrated or depleted at that point. However, one can not use the sign of Laplacian itself since it is dominated by the charge of nuclei. Instead the sign of the Laplacian along the axes of its maximum variation must be analyzed, which is given by the second eigenvalue λ_2 of the Hessian matrix of the electron density ($\lambda_1 < \lambda_2 < \lambda_3$). Indeed, λ_2 can be either positive or negative, distinguishing between bonding interactions, such as hydrogen bonds, characterized by a charge accumulation ($\lambda_2 < 0$) or non-bonding interactions, such as steric repulsions, characterized by a charge depletion ($\lambda_2 > 0$). Finally, van der Waals interactions are characterized by a negligible density overlap that gives $\lambda_2 \lesssim 0$. Thus, the analysis of the sign of λ_2 enables to distinguish different types of weak interactions, while the density itself enables to access the interaction strength. Hence, $\lambda_2 n(\mathbf{r})$ is used as a colorscale for the RDG isosurfaces.

1.2.6 DENSITY FUNCTIONAL PERTURBATION THEORY

Density Functional Perturbation Theory (DFPT) [24] is a method to compute linear response properties of the system to an external perturbation, starting from the ground state solution of the Kohn-Sham problem. In DFPT, the responses to perturbations of different wavelengths are decoupled, allowing to calculate phonon frequencies at any wave vector $\mathbf{q}$ without the use of supercells and with a computational cost independent of the phonon wavelength.

For a system near its equilibrium geometry, the harmonic approximation applies, and the nuclear Hamiltonian reduces to the Hamiltonian of a system of independent harmonic oscillators, referred to as normal modes. Normal mode frequencies ω , and displacement patterns, denoted as U^α for the α -th Cartesian

component of the I -th atom, are determined by the secular equation:

$$\sum_{J,\beta} \left(C_{IJ}^{\alpha\beta} - M_I \omega^2 \delta_{IJ} \delta_{\alpha\beta} \right) U^\beta = 0 \quad (1.59)$$

where M_I is the ionic mass and $C_{IJ}^{\alpha\beta}$ is the Interatomic Force Constant (IFC) matrix element defined by:

$$C_{IJ}^{\alpha\beta} = \frac{\partial^2 E(\{\mathbf{R}\})}{\partial R_I^\alpha \partial R_J^\beta} = -\frac{\partial F_I^\alpha}{\partial R_J^\beta}. \quad (1.60)$$

Here R_I^α are the displacements of atom I along direction α . Applying the Hellmann-Feynman theorem, the forces F_I^α can be calculated by means of a simple derivation of the energy functional with respect to the atomic positions:

$$F_I^\alpha = -\frac{\partial E}{\partial R_I^\alpha} = -\int d\mathbf{r} \frac{\partial v_{ext}(\mathbf{r})}{\partial R_I^\alpha} n(\mathbf{r}) - \int d\mathbf{r} \frac{\delta E}{\delta n(\mathbf{r})} \frac{\partial n(\mathbf{r})}{\partial R_I^\alpha} - \frac{\partial E_{ion}}{\partial R_I^\alpha} \quad (1.61)$$

where the second term vanishes being in a minimum of the energy with respect to the charge distribution. By performing an explicit differentiation of the forces with respect to nuclear coordinate can be obtained the following expression for IFC:

$$C_{IJ}^{\alpha\beta} = \int d\mathbf{r} \frac{\partial n(\mathbf{r})}{\partial R_J^\beta} \frac{\partial v_{ext}(\mathbf{r})}{\partial R_I^\alpha} + \delta_{IJ} \int d\mathbf{r} \frac{\partial^2 v_{ext}(\mathbf{r})}{\partial R_I^\alpha \partial R_J^\beta} n(\mathbf{r}) + \frac{\partial^2 E_{ion}}{\partial R_I^\alpha \partial R_J^\beta} \quad (1.62)$$

In order to obtain the IFC matrix elements, the linear variation of the charge density with respect to the atomic displacements must be computed. This is obtained from eq. (1.16):

$$\frac{\partial n(\mathbf{r})}{\partial R_I^\alpha} = 2 \sum_i f_i \psi_i^*(\mathbf{r}) \frac{\partial \psi_i(\mathbf{r})}{\partial R_I^\alpha} \quad (1.63)$$

and the derivatives of the KS wavefunctions are similarly obtained from eq. (1.17):

$$\left(\hat{H}_{KS} - \epsilon_i \right) \frac{\partial \psi_i(\mathbf{r})}{\partial R_I^\alpha} = - \left(\frac{\partial v_{KS}(\mathbf{r})}{\partial R_I^\alpha} - \frac{\partial \epsilon_i}{\partial R_I^\alpha} \right) \psi_i(\mathbf{r}) \quad (1.64)$$

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where

$$\frac{\partial v_{KS}(\mathbf{r})}{\partial R_I^\alpha} = \frac{\partial v_{ext}(\mathbf{r})}{\partial R_I^\alpha} + e^2 \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \frac{\partial n(\mathbf{r}')}{\partial R_I^\alpha} + \int d\mathbf{r}' \frac{\delta v_{xc}(\mathbf{r})}{\delta n(\mathbf{r}')} \frac{\partial n(\mathbf{r}')}{\partial R_I^\alpha}. \quad (1.65)$$

The last three equations defines a self-consistent problem. From the ground state energy, a linear variation of the charge is calculated for a specific mode (defined by a set of nuclear translations). The linear variations of the wavefunctions can be calculated, and the potential is updated. This process can iterate until the desired precision is achieved.

1.3 MACHINE LEARNING APPROACHES

DFT-based methods can provide highly accurate predictions for a wide range of material properties. However, they require a high computational cost, limiting their applicability to systems with up to approximately 1000 atoms. Notably, Ab Initio Molecular Dynamics (AIMD) calculations, which involve performing a full SCF to obtain energy and forces for each MD step, are particularly demanding. Consequently, they can only be feasibly conducted on short timescales of around 100 ps. However, many intriguing phenomena, such as phase transitions, chemical reactions, or the study of defected materials and surface reconstructions, require longer timescales and larger simulation cells.

Conversely, classical molecular dynamics enables more extensive and longer simulations at a significantly lower computational cost. Nevertheless, the accuracy of the results is constrained by the empirical potentials used to describe interatomic interactions.

In this context, Machine Learning (ML) approaches can offer a solution to overcome these limitations. Specifically, ML models can be trained using a sufficient amount of DFT data to learn the underlying Potential Energy Surface (PES). Subsequently, the learned Interatomic Potential (IP) can be employed in classical molecular dynamics simulations, effectively combining the accuracy of DFT with the computational efficiency of classical molecular dynamics.

Indeed, the training of a ML IP aims to find a mapping from atomic positions $\{\vec{r}_i\}$ and the chemical species $\{Z_i\}$ to the potential energy $\{E_{pot}\}$ and forces acting on each atom $\{\vec{F}_i\}$. In doing that several key assumptions are made. One of these assumptions is that the energy of the system can be expressed as a sum of atomic contributions $E_{pot} = \sum_{i=1}^N E_i$. Another fundamental assumption is that

these atomic energies are dependent on the local environment surrounding each atom. Specifically, the energies are influenced by the presence of neighboring atoms within a defined radial cutoff distance denoted as r_c .

Forces are then obtained as the gradient of the predicted total potential energy with respect to the atomic positions $\vec{F}_i = -\nabla_i E_{pot}$.

Among the many codes available for the construction of ML IP, two of them were tested here, DeePMD and NequIP.

1.3.1 DEEPMD

The DeePMD package [25, 26] is built upon TensorFlow, one of the most popular deep learning frameworks, and employs a fully connected neural network. To preserve the physical invariance properties of the system, in particular translational, rotational, and permutational invariance, a preprocessing step is applied to the atomic positions before the fitting network. In this process, an encoding Deep Neural Network (DNN) is utilized to transform the atomic positions into specialized descriptors that capture the atomic chemical environment while preserving all relevant symmetries.

These descriptors are designed to encode either radial information, which involves the relative distances between atoms, or a combination of radial and angular information. However, it is worth noting that physical intuition suggests that interactions such as covalent bond stretching, bending, and dihedral angle forces are best described by considering the complete coordinate information of the first two neighboring shells in the input data. In contrast, long-range interactions, such as van der Waals effects, are adequately captured by a radial descriptor for more distant neighbors. As a result, for the sake of efficiency, it is typically sufficient to incorporate both angular and radial information for the closest neighbors within a specified neighbor shell, while using radial-only information for the remaining neighbors within a second cutoff radius [25].

1.3.2 NEQUIP

NequIP is instead based on Torch framework implementing a Graph Neural Network (GNN). The topology of such a GNN, is constructed in such a way to reflect the atomistic crystal structure. Indeed, atomic structures are represented by collections of nodes and edges, where nodes in the graph correspond to

1.3. MACHINE LEARNING APPROACHES

individual atoms and edges are defined by simply connecting every atom to all other atoms that are closer than some cutoff distance r_c . Above this architecture, Message Passing Neural Network (MPNN) framework [27] is introduced as a common GNN paradigm for atomistic structures.

Indeed, within an atomistic GNN, the atoms and their connections are associated with numerical lists of *features*. These features are updated by the Message Passing framework in a two step process. In the first step, each atom receives a message that is an aggregate of its neighbor’s features. In the second step, the updated features of an atom are evaluated, by means of a function that depends on the message received and the atom’s own features. By iterating that scheme n times, each atom will receive messages from atoms that are distant up to n connections, thus accounting for long-range interactions [28].

In contrast to DeePMD, NequIP uses relative position *vectors* rather than simply distances (scalars) together with features comprised also of high order geometric tensors. This makes the internal features equivariant to rotation and reflection. Even though the output is the predicted potential energy E_{pot} , which is invariant under translations, reflections, and rotations, the network contains internal features which are equivariant to symmetry operations. In that way, equivariant neural networks guarantee to preserve the transformation properties of physical systems.

1.3.3 TRAINING DATASET

The architecture of the network is of great importance to build accurate models; however, in order to train a model, it is of paramount importance to have an extensive dataset of high-quality data. A common method, used to generate the configurations used in this work, is to create a small set by means of ab initio Born-Oppenheimer Molecular Dynamics (BOMD) at different thermodynamic conditions and then use this dataset in an active learning approach consisting of repeated cycles of exploration, labeling, and retraining of the model:

- **Exploration:** after a first training, the model is used in classical molecular dynamics to generate new configurations.
- **Labeling:** for a few selected configurations, ab initio energy and forces are then computed by means of DFT calculations.
- **Retraining:** the model is retrained with the new data, and the cycle is repeated.

This method is particularly efficient since, during the exploration phase by means of *ab initio* or classical molecular dynamics, atomic positions at each step are highly correlated with the previous ones, so that, to avoid overfitting, only one configuration every ~ 100 is used for the training. Hence this method permits to generate long trajectories at low cost with classical simulations and label just a few of them with DFT calculations.

2

Tetra-pyridyl porphyrins at surfaces

2.1 BACKGROUND

Catalysis plays a pivotal role in various sectors, serving as a cornerstone of chemical, industrial, and environmental processes. Its importance is evident in industries like pharmaceuticals, chemicals, and energy production, where catalysis is used to enhance efficiency and product quality. Indeed, catalytic materials have the ability to accelerate chemical reactions by reducing the activation energy required for these reactions to proceed. However, catalytic processes can be influenced by many factors. First of all they can be generally categorized into two distinct families: homogeneous and heterogeneous.

In homogeneous catalysis, both the catalyst and the reactants exist in the same phase, typically in a solution. These reactions often exhibit higher selectivity, but they can be challenging when it comes to separating the catalyst from the reaction products.

Conversely, in heterogeneous catalysis, the catalyst is in a different phase from the reactants. This typically involves scenarios like solid-gas or solid-liquid reactions. Heterogeneous catalysis is more commonly employed due to the ease of separating the reaction products from the catalyst.

The size of the catalyst is another critical factor that significantly influences catalytic activity. In many practical applications, metallic nanoclusters are preferred as catalysts due to their high surface-to-volume ratio. Smaller catalyst sizes often result in a higher proportion of low-coordinated atoms, which are

2.1. BACKGROUND

typically highly reactive [29]. Additionally, at the nano or subnano scales, quantum effects come into play, further altering the catalytic properties. However, synthesizing these nanoclusters is challenging, and their stability is often a concern. Temperature and pressure can lead to sintering, causing a loss of catalytic activity. Furthermore, due to the size's crucial role, controlling the cluster size is essential to achieve high selectivity and prevent the formation of unwanted products.

In this context, the use of a Single Atom Catalyst (SAC) represents the ideal solution. In SACs, isolated catalytic metallic atoms are dispersed on a suitable support to prevent clustering. The presence of single metal atoms optimizes the metal usage and its specific activity. It also allows for fine-tuning control at a fundamental level, ensuring that all active sites are identically coordinated, resulting in the same catalytic properties throughout the catalyst.

As mentioned, a major challenge is the preparation of SACs while stabilizing these single atoms to prevent their aggregation. A promising method for achieving this is the stabilization of the metal center by an organic matrix or cage, leading to the formation of so-called Metal-Organic Framework (MOF)s. These compounds are characterized by a high degree of crystallinity and possess many degrees of freedom that can be exploited to tune the catalytic selectivity of the system. These tunable factors include the substitution of metallic atoms, the possible presence of non-equivalent sites, or the usage of different ligands. Furthermore, since these systems are usually bidimensional, they need to be supported by an appropriate substrate. Hence, the substrate itself can modify the MOF properties by means of the surface trans-effect, namely, such as appends in the molecular trans-effect, the substrate can act as a trans ligand influencing the lability of additional ligands on top of the molecular layer.

The study described in this chapter is situated in this context, and among the various MOFs suitable for heterogeneous catalysis, the focus was on porphyrin-based metallorganic layers.

Porphyrins are a class of organic molecules characterized by a macrocyclic structure composed of four pyrrole rings linked by methine bridges ($=CH-$) (fig. 2.1, panel A). The porphyrin ring is a versatile ligand that can bind to a variety of metal atoms, including iron, cobalt, copper, manganese. The resulting metalloporphyrins are widely present in nature covering a wide range of fundamental biological tasks, ranging from molecular transport to energy conversion [30, 31, 32]. These compounds are also widely studied due to the broad range

of potential applications not only in catalysis but also for organic solar cells, spectroscopic markers, sensors, and switches [33, 34, 35, 36].

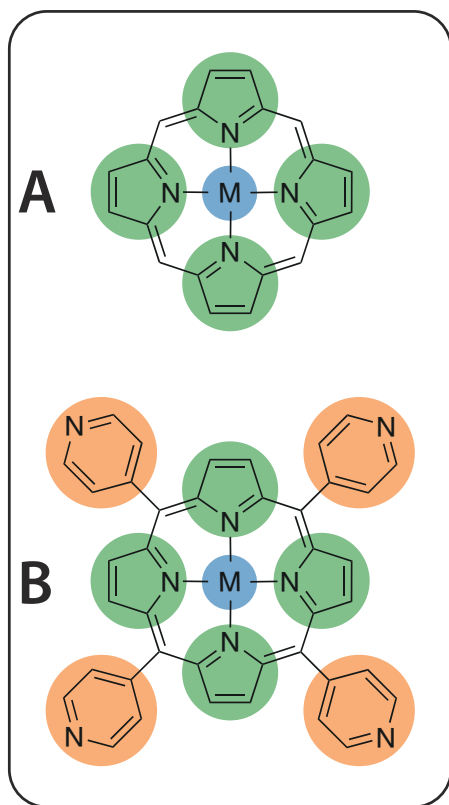


Figure 2.1: Skeletal representation of: A) metallo-porphyrin molecule, B) metallo-tetra-pyridyl porphyrin molecule. The metal atom M is represented in blue, the pyrrole rings in green, the pyridinic rings in orange.

Those molecules are particularly suitable since they can bind different peripheral meso-substituents. Molecules with particular substituents were shown to be ideal building blocks for the self-assembly of highly ordered two-dimensional architectures at surfaces [30, 37, 38, 39]. The resulting patterns observed to form on many metallic substrates arise from the balance between the interaction of each molecule with the substrate and its neighboring molecules [39]. The specificity of the substrate, and in some cases even the characteristics of the adsorption sites, combined with the molecular end-groups, determine the structure of the self-assembled pattern. For the work presented here, were considered 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP) with a single Co atom caged in the porphyrinic macrocycle (CoTPyP)

and functionalized by four pyridinic end-groups (fig. 2.1, panel B). If additional metal atoms (generally of a different species than the one already present inside the macrocycle) are added to the system, they can occupy the intermolecular sites between four adjacent pyridinic rings, leading to the formation of a bimetallic layer. The resulting structure is a MOF usually with different periodicity compared to the monometallic case, where only a metal atom is caged inside the porphyrinic core. In this way, the outer groups become crucial for both the geometry of the molecular layer and the tuning of porphyrin's electronic properties.

2.2. GEOMETRICAL STRUCTURE

In the present study both monometallic (CoTPyP) and bimetallic (CoTPyP-Co) layers are investigated.

Furthermore, as mentioned, the substrate also plays a fundamental role due to a charge transfer effect with the molecular layer. [40, 41, 42]. Here the substrate considered is Graphene (GR) on a (111)-terminated Ir surface. GR, as will be shown in the following, was chosen for the low interacting nature both with iridium and with the molecular layer, allowing to focus on the intrinsic properties of the molecular layer.

The chapter is divided into three main parts. The first part mainly involves a structural characterization of the different molecular layers and delves into the driving forces behind the self-assembly process. The second part is dedicated to the electronic and chemical properties of the system, particularly in the context of catalytic applications. Finally, the last part is dedicated to the investigation of reactivity, particularly considering the adsorption of CO and the stabilization of the OOH-H₂O complex.

2.2 GEOMETRICAL STRUCTURE

2.2.1 THE SUBSTRATE: GRAPHENE/IRIDIUM(111)

To reduce computational complexity, the initially explored assumption was that the presence of the iridium substrate has a limited influence on the molecular adlayer due to the low interaction between GR and Ir(111). This would allow to model the system by considering only the graphene layer and the adsorbed CoTPyPs.

Graphene and Ir(111) exhibit slightly different lattice constants. The computed lattice parameter for graphene is 2.460 Å, whereas for bulk Ir, it is 3.847 Å, which corresponds to a 2.720 Å lattice parameter for Ir(111). This leads to the formation of a Moiré pattern with a 0.9 ratio between the two lattice constants. To model this, a supercell consisting of a 10 × 10 unit cell of graphene and a 9 × 9 unit cell of Ir was used, with no rotational angle between them. This resulted in a slight compression of the graphene layer, with a new lattice parameter of 2.449 Å. The resulting supercell had a lattice parameter of 24.49 Å, consistent with the periodicity of approximately 25 Å observed in STM images (see fig. 2.2).

The semi-infinite Ir(111) substrate was represented by a slab consisting of 3 Ir layers. The bottom layer was fixed at the bulk position, while the top two layers

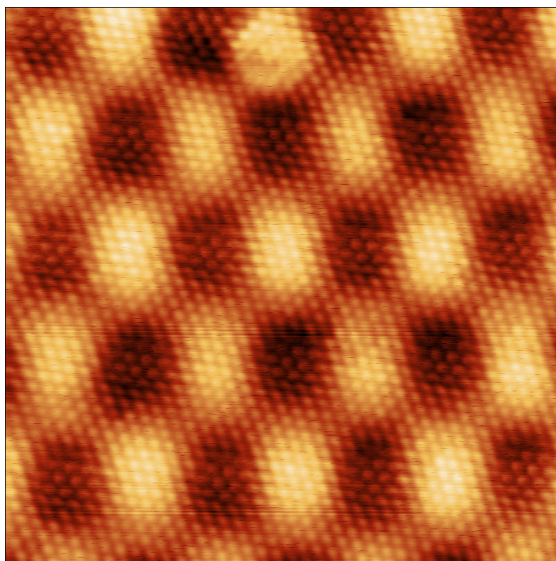


Figure 2.2: STM image of bare graphene acquired at -150 mV and 1.2 nA, image size $9 \times 9 \text{ nm}^2$

were allowed to relax. Graphene was added only on the free Ir termination and was allowed to optimize atomic positions. Due to the asymmetry along the z-axis, there was a non-physical dipole moment between the two sides of the slab originating from subsequent replicas of the cell. To compensate for this effect, a dipole correction was applied to the system. Given the large unit cell, only the Gamma point was considered for Brillouin zone integration.

After relaxation, the small compression of graphene led to a slight corrugation of the adlayer, with an average distance from the substrate of $3.45 \text{ \AA}$ (see fig. 2.3 panel A). Due to the lattice mismatch, three regions with different local registry were identified, characterized by the relative positions of the center of graphene hexagonal rings with respect to Ir atoms on the substrate. The fcc and hcp regions, which are very similar (they differ only for the position of atoms in the second Ir layer), are the closest to the substrate, while the atop region is the most distant.

Next, a single CoTPyP molecule was adsorbed on this optimized substrate. Full relaxation showed that the graphene buckling amplitude remained largely unaffected, as did the distances from the iridium substrate, except for a slight decrease of $0.02 \text{ \AA}$ under the molecule (see fig. 2.3 panel B). Furthermore, no pinning of graphene occurred, in contrast to phthalocyanine molecules on the same metallic surface, where isoindole units were observed to push GR towards Ir [43].

2.2. GEOMETRICAL STRUCTURE

Moreover, when comparing the optimized structure of a single CoTPyP molecule on GR/Ir(111) with one on free-standing GR (to be discussed in the next section), was observed that the geometrical conformation of CoTPyP was not significantly affected by the presence of the substrate. This finding aligns with a previous study indicating a low interaction between graphene and the iridium substrate [44]. Therefore, GR can be regarded as a decoupling layer between the substrate and the molecular adlayer, allowing to model the system while neglecting Ir(111) and focusing solely on CoTPyP molecules adsorbed on graphene.

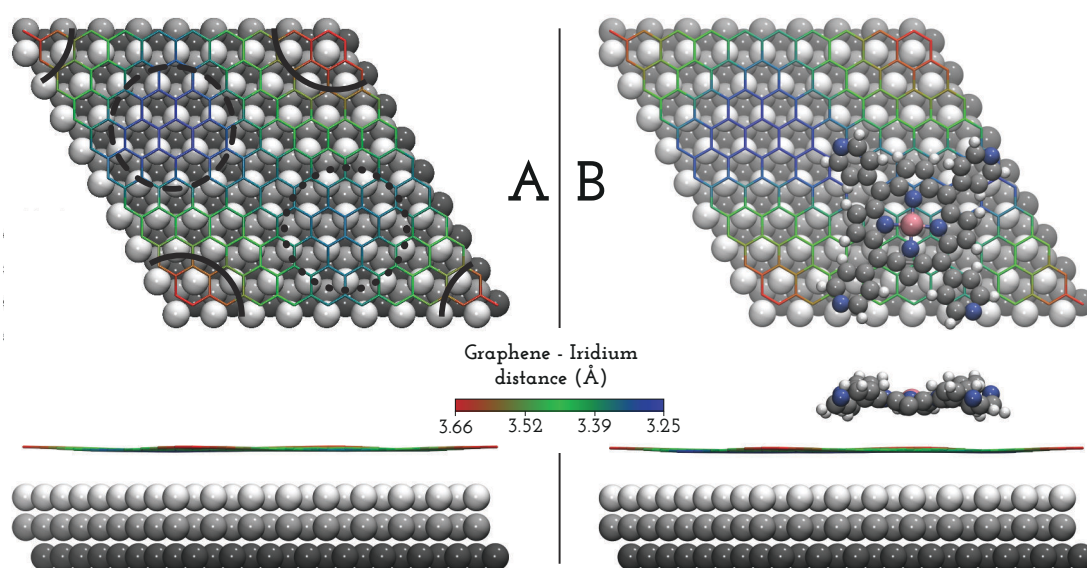


Figure 2.3: Optimized structure for Graphene buckling on Ir(111) surface. A) Top and side views for bare graphene on Iridium (111). In the top view are marked the fcc (dashed line), hcp (dotted line) and ontop (solid line) adsorption registers of GR. B) Top and side views with and additional CoTPyP molecule adsorbed on GR/Ir(111). Graphene color scale highlights the distance from the Ir substrate.

2.2.2 STANDALONE CoTPyP MOLECULE

As our initial foray into exploring the complete molecular layer, we commence by examining the adsorption of a standalone CoTPyP molecule on a GR substrate. This choice enables to center the attention on the interaction between the molecule and the substrate, differentiating it from the influence of intermolecular interactions within the adsorption geometry.

Here was considered a slab simulation cell (15 Å high) with rectangular base sufficiently large to leave at least 4 Å between the molecule and its periodic images, in order to avoid spurious interactions, allowing to consider the molecule as isolated. This unit cell contains 56 graphene units with 2.46 Å lattice parameter and has in plane dimensions of 17.22 Å × 17.04 Å.

Depending on the adsorption substrate, porphyrin-based molecules can adopt varying conformations. On strongly interacting substrates, they tend to lie perfectly flat, assuming a D_4 symmetry, as demonstrated by the example of Zn-tetra-phenyl porphyrins on Ag(110) [45]. However, on substrates with weaker interactions, a multitude of conformations becomes observable.

In the case of CoTPyP molecules on graphene, our predictions suggest that they will adsorb with a C_{2v} symmetry. This configuration features a macrocycle that is distinctly *saddle-shaped*, with tilted peripheral pyridinic rings. This is visually represented in fig. 2.3 and fig. 2.4.

This particular adsorption geometry is not unique to CoTPyP; it has been previously observed with different porphyrin-based molecules on various substrates, such as Cu(111) [46] and Au(111) [47]. Additionally, similar configurations have been observed for porphyrins with different peripheral end-groups [45].

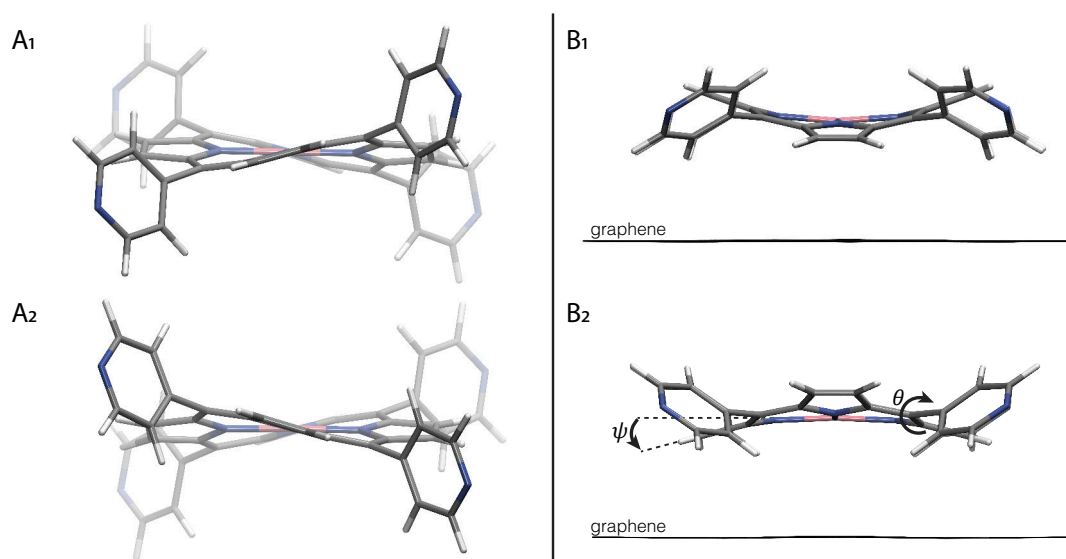


Figure 2.4: Optimized structure of a single molecule in gas phase and adsorbed on graphene. The angles θ and ψ describe respectively the rotation of the pyridinic groups respect to a vertical plane passing through the Co atom and the pyridinic N atom, and the rotation of the pyrroles respect to the graphene plane.

2.2. GEOMETRICAL STRUCTURE

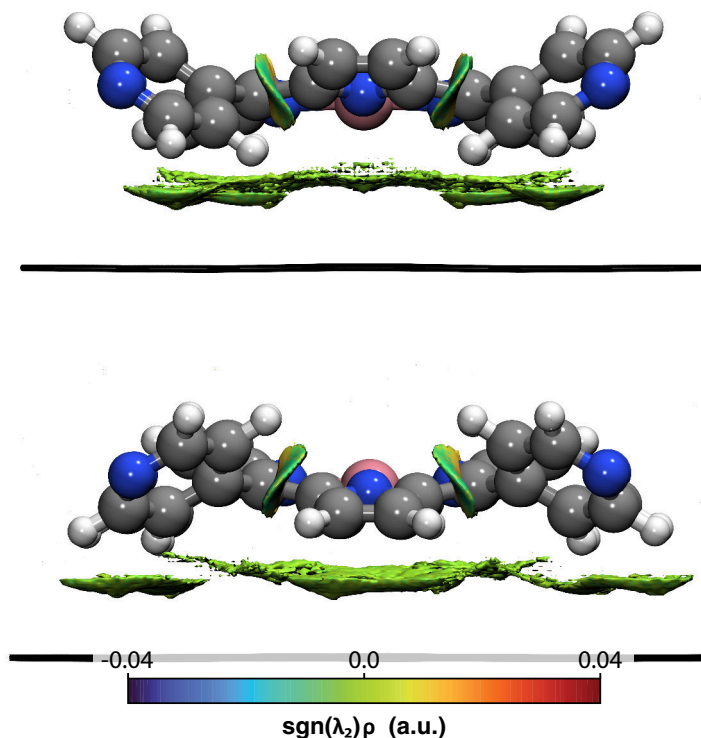


Figure 2.5: Visualization of non-covalent interactions by means of RDG isosurfaces along two different side views. The isosurfaces are plotted at 0.6 a.u. and colored according to the sign of the second eigenvalue of the Laplacian of the electron density.

To gain a clearer understanding of the role of the substrate in determining the adsorption geometry, the adsorbed molecule was compared to the free-standing CoTPyP molecule shown in fig. 2.4. This comparison reveals that the substrate's influence acts as a compromise. It encourages the pyridinic groups and the macrocycle to lie as flat as possible, while also introducing steric repulsion between the iminic and pyridinic hydrogens, causing the molecule to bend.

These interaction regions are highlighted in fig. 2.5, where RDG isosurfaces are plotted. It is evident from these figures that the low charge density between the molecule and the substrate confirms the presence of weak interactions dominated just by hydrogen and van der Waals forces. Conversely, the steric coupling between the iminic and pyridinic hydrogens exhibits a slightly higher charge density in the interaction region, suggesting a somewhat stronger interaction in this area.

These forces induce a distortion in the porphyrinic ring, with the two pairs of opposite pyrroles inclined towards or away from the surface by approximately

$\psi \simeq \pm 18^\circ$. Meanwhile, the pyridinic groups exhibit an alternating clockwise and counterclockwise rotation of approximately $\theta \simeq 38^\circ$ concerning the orientation relative to graphene.

The extent of this saddle-shaped distortion varies depending on the strength of the substrate-adsorbate interaction. For example, when considering MnTPyPs on the more strongly interacting Cu(111) substrate, the pyridinic groups and the pyrroles pointing downwards tend to be flatter, with $\theta = 29.8 \pm 1.8^\circ$ and $\psi = -14.6 \pm 0.9^\circ$, while the pyrroles pointing upwards are more inclined ($\psi = 24.7 \pm 1.5^\circ$) [48]. A similar angle of $\theta = 30 \pm 5^\circ$ was predicted for 2HTPyPs on Ag(111) [47].

In our specific case, the Co metal atom has a distance of 3.8 Å from the substrate, and the minimum distance between the hydrogen terminations and the substrate is approximately 2.5 – 2.6 Å. These distances are comparable to those observed for H-H steric interactions and are also consistent with values observed for other molecules with cyclic groups [49].

The calculated adsorption energy per molecule amounts to $E_{ads} = -1.95$ eV, encompassing contributions from hydrogen bonds and van der Waals interactions. This energy was computed as the difference in total energy between the whole system and the two components (GR and CoTPyP) separately simulated. Notably, there is no noticeable predilection for particular adsorption sites or registries. Rotations or translations parallel to the GR plane do not induce changes in the molecular structure or the adsorption energy. These characteristics suggest ideal conditions for diffusion and self-assembly.

Following the adsorption of CoTPyP, graphene retains its perfectly flat structure, and there is no observable charge transfer between the molecule and GR fig. 2.6. Consequently, the DoS of graphene remains unaltered, with the Dirac points situated at the Fermi energy level. Thus, graphene primarily functions as a weakly interacting substrate for the isolated molecule, playing a role in shaping its geometric conformation and causing minimal charge rearrangement, as depicted in fig. 2.6. This rearrangement of charge was obtained by means of an electron density difference between the whole CoTPyP/graphene system and the isolated graphene and CoTPyP molecules at fixed atomic positions.

2.2. GEOMETRICAL STRUCTURE

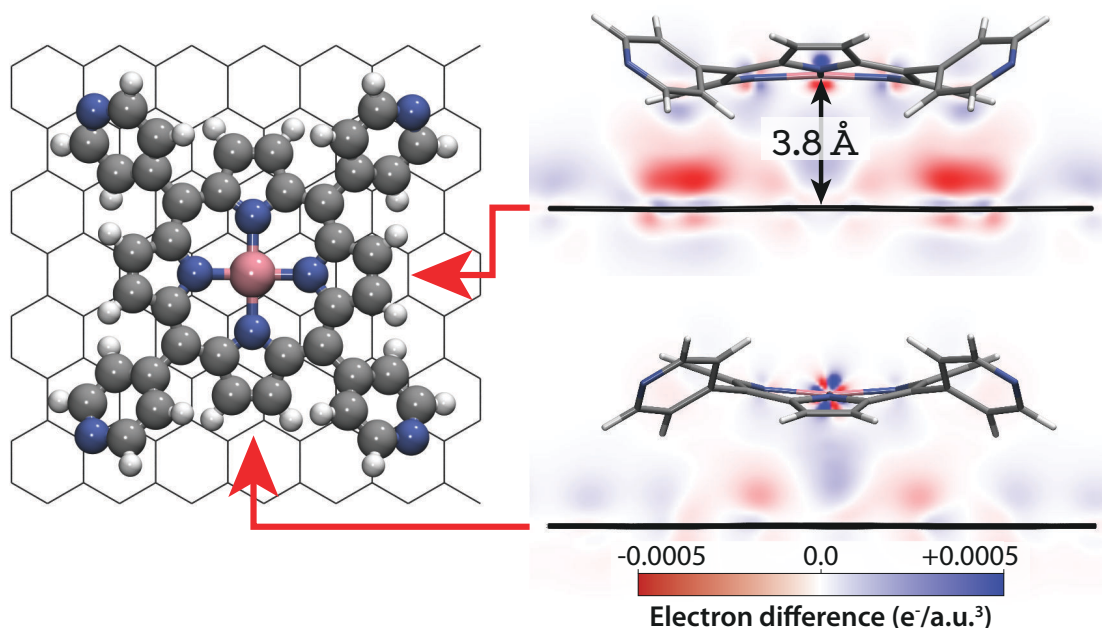


Figure 2.6: Individual CoTPyP molecule adsorbed on graphene: optimized DFT model (ball-and-stick rendering for the top view; sticks only for the two side views), taken in the directions indicated by the arrows, with the calculated electron density rearrangement due to the interaction of the molecule with GR plotted on the reflection symmetry planes of the molecule passing through the Co atom and perpendicular to GR.

2.2.3 MONOMETALLIC CoTPyP LAYER

Upon evaporating CoTPyP molecules onto a graphene/iridium(111) substrate under carefully controlled experimental conditions, these molecules undergo spontaneous self-assembly into a well-ordered two-dimensional molecular layer. This phenomenon is readily evident in the STM images showcased in fig. 2.7, where the formation of large islands, spanning hundreds of nanometers, becomes apparent.

This observation provides further confirmation of the findings presented in the preceding chapter, emphasizing the presence of a weak interaction between these porphyrins and the substrate. This weak coupling enables high mobility and the remarkable self-assembly capability of the molecules.

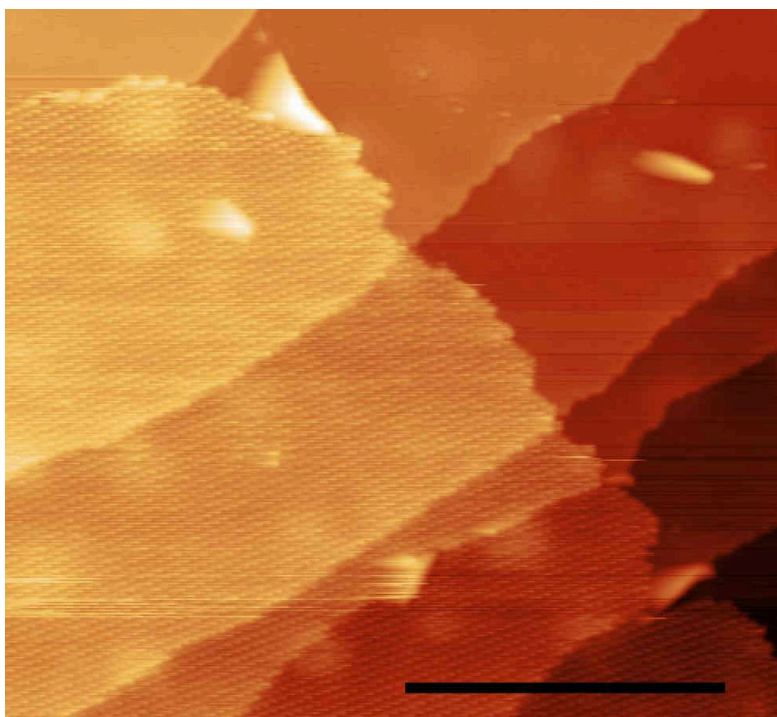


Figure 2.7: Large scale STM image for a monolayer of CoTPyP/GR/Ir(111) acquired at 77 K and $I = 0.1$ nA and $U_{bias} = +2.0$ V. The large CoTPyP islands are visible, indicating the high porphyrin mobility on GR during the deposition process. (Scale bar = 50 nm)

Zooming in with smaller-scale STM topographic images taken under negative bias (see fig. 2.8, Panel B), a staggered arrangement emerges, comprising rows of molecules with alternating orientations. To emphasize this staggered pattern, the molecule orientations were highlighted with "H" shapes in fig. 2.8. Within each row, the molecules are simply translated, but in the adjacent row, they exhibit a different azimuthal orientation. This results in the creation of specific chiral domains. The molecular centers within this structure collectively form an almost hexagonal pattern. Described as an oblique lattice with cell parameters $a = 31.0$ Å, $b = 14.8$ Å, and $\alpha = 63.8^\circ$, it accommodates two non-identical CoTPyP molecules per unit cell, rotated relative to each other by an azimuthal angle of 65° .

Similar densely packed structures have been observed in the past, such as those formed by 2HTPyPs on Ag(111) [47], FeTPyP on Au(111) [50], or tetraphenylporphyrins on Ag(111) [51].

In order to understand the origin of the molecular packing, in fig. 2.9 were plotted the four interacting regions responsible for the self-assembly of CoTPyP

2.2. GEOMETRICAL STRUCTURE

molecules. Two of these regions (labeled as A), previously noted discussing the standalone CoTPyP/GR, are responsible for the molecular ‘saddle shape’ and the rotation of the peripheral residues. The other two regions take advantage from this conformation to facilitate self-assembly and involve interactions with two adjacent molecules. In one case (Region B), the interaction involves just one neighboring peripheral residue, while in the other (Region C), it becomes more intricate, encompassing both a pyridinic and iminic ring belonging to a molecule in the adjacent row.

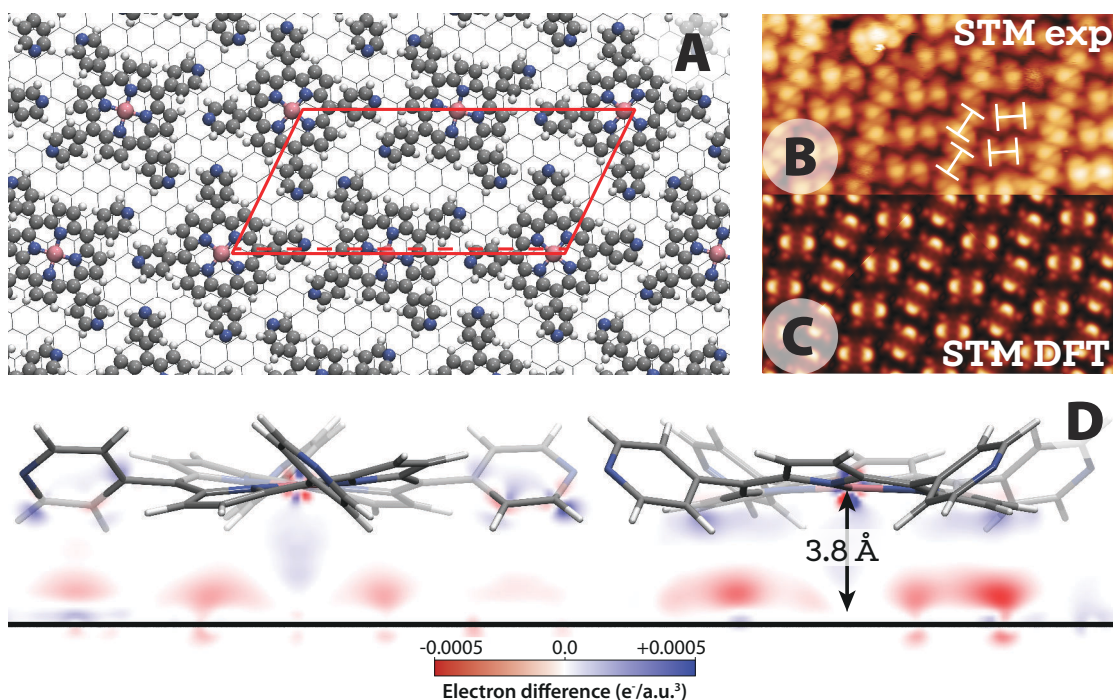


Figure 2.8: Monometallic CoTPyP molecular layer: A) Optimized DFT model (ball-and-stick rendering for the top view, with the supercell used; sticks only for the side view); B) Experimental STM image acquired at $I = 100\text{pA}$ and $U_{bias} = -2.0\text{V}$. "H" shapes highlight the orientation of the molecules; C) DFT simulated STM image computed at constant high of $2.25\text{ \AA}$ above Co atoms; D) Plot of the calculated electron density rearrangement due to the interaction between the molecular layer and GR on a plane perpendicular to GR and passing through the Co atoms of two adjacent molecules, parallel to the long side of the supercell (dashed red line).

The latter two regions play a pivotal role in establishing the staggered arrangement, as they induce a relative rotation of the molecules to one another. Notably, the interaction energy associated with this arrangement was quantified

at $E_{\text{int}} = -0.41$ eV per molecule ¹, meaning that each pyridinic ring contributes approximately $E_{\text{int}}/4 = -0.1$ eV. This observation aligns with the relatively large H-X (where X represents C or N atoms) distances, exceeding 3.2 Å, and the low charge density within the interaction region, measuring less than 0.01 atomic units (fig. 2.9) [52].

Simultaneously, DFT results indicate that the interaction between a molecule within a self-assembled layer and the substrate is not significantly different from the scenario of an isolated molecule. There is no discernible charge transfer; instead, just a minor redistribution of charge is observed (fig. 2.8, Panel D). Similar to the previous case, the distance between the molecule and the substrate remains unchanged.

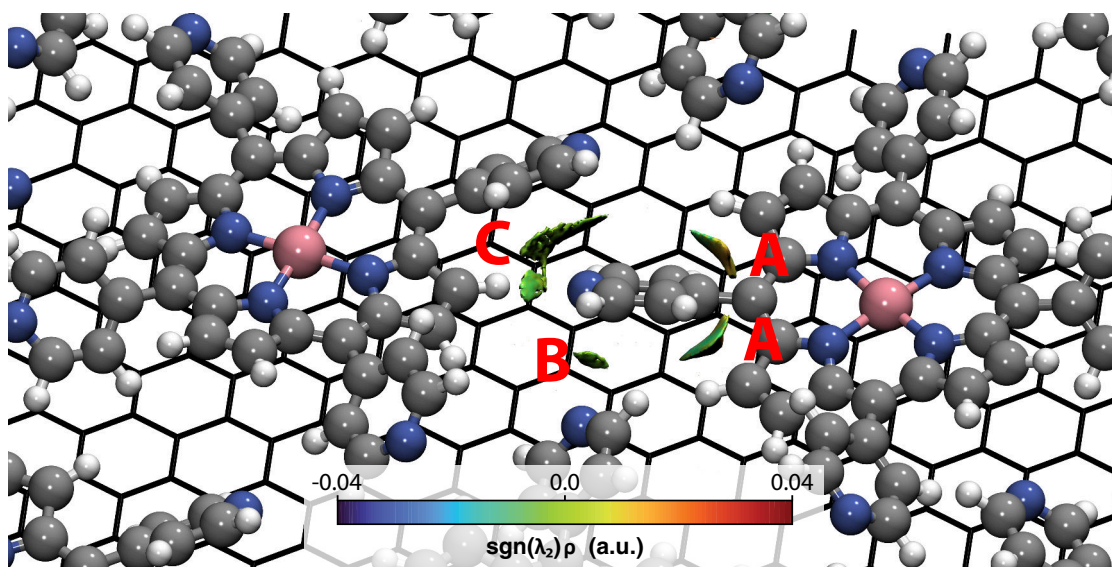


Figure 2.9: Non-covalent interacting regions responsible for the self-assembly of CoTPyP molecules. For clarity, the interacting regions between involving just one pyridinic ring are shown. The RDG isosurfaces are plotted at 0.6 a.u. and colored according to the sign of the second heigenvalue of Laplacian of the electron density.

The calculated adsorption energy for each molecule is $E_{\text{ads}} = -1.72$ eV, only slightly weaker than the case of a single isolated molecule. Furthermore, the geometric conformation of an adsorbed molecule, whether isolated or within

¹The lateral intermolecular energy was estimated as the total energy of the molecular layer (neglecting for GR) normalized by the number of molecules and the energy of a single isolated molecule in vacuum. Both layer and single CoTPyP are considered fixed at the relaxed atomic position they exhibit on GR.

2.2. GEOMETRICAL STRUCTURE

a molecular layer, remains consistent. In this case as well, neither specific adsorption sites nor a registry with GR have been identified, neither in the experimental STM images nor in the DFT calculations. This suggests that the self-assembly process is exclusively driven by lateral intermolecular interactions.

2.2.4 BIMETALLIC CoTPyP-Co LAYER

In this section, will be explored the formation and characterization of the bimetallic CoTPyP-Co layer. To quantify the presence of peripheral Co atoms, will be used the parameter Θ , defined as $\Theta = \frac{\theta_{Co}}{\theta_{CoTPyP}}$, where θ_{Co} represents the number of peripheral Co atoms, and θ_{CoTPyP} represents the number of CoTPyP molecules per unit area.

Our investigation will commence with a study of partial coverage by Co atoms, enabling to understand the dynamic process involved in the formation of the bimetallic layer. Subsequently, will be delved into an examination of the CoTPyP-Co system at full coverage.

UNSATURATED CoTPyP-Co LAYER

STM images reveal a remarkable transformation in the molecular arrangement upon the deposition of Co atoms onto the CoTPyP layer. This transformation alters the arrangement from a hexagonal pattern to an almost square lattice.

At low Co coverage ($\Theta \lesssim 0.25$), the Co atoms on the surface bind with four CoTPyPs through their pyridinic terminations to achieve tetra-coordination. Consequently, these four molecules are compelled to rearrange their relative positions, forming a rigid, nearly square (CoTPyP)₄Co block (fig. 2.10, Panel A). This configuration is now favored over a previously observed close-packed structure where direct lateral interactions between molecules existed. Interestingly, on a more interactive substrate, such as Au(111), additional metals can coordinate similarly in a fourfold manner, but only when the molecules are preassembled in a nearly square lattice [53].

The STM image reveals also that the block has a precise chirality, due to a specific orientation of the four CoTPyP molecules, which are rotated by 90° one with respect to the neighboring ones, as highlighted by the "H"-like shapes. This arrangement is enforced by steric interactions among peripheral residues pointing to the Co atom. In order to maximize their relative distances, they all

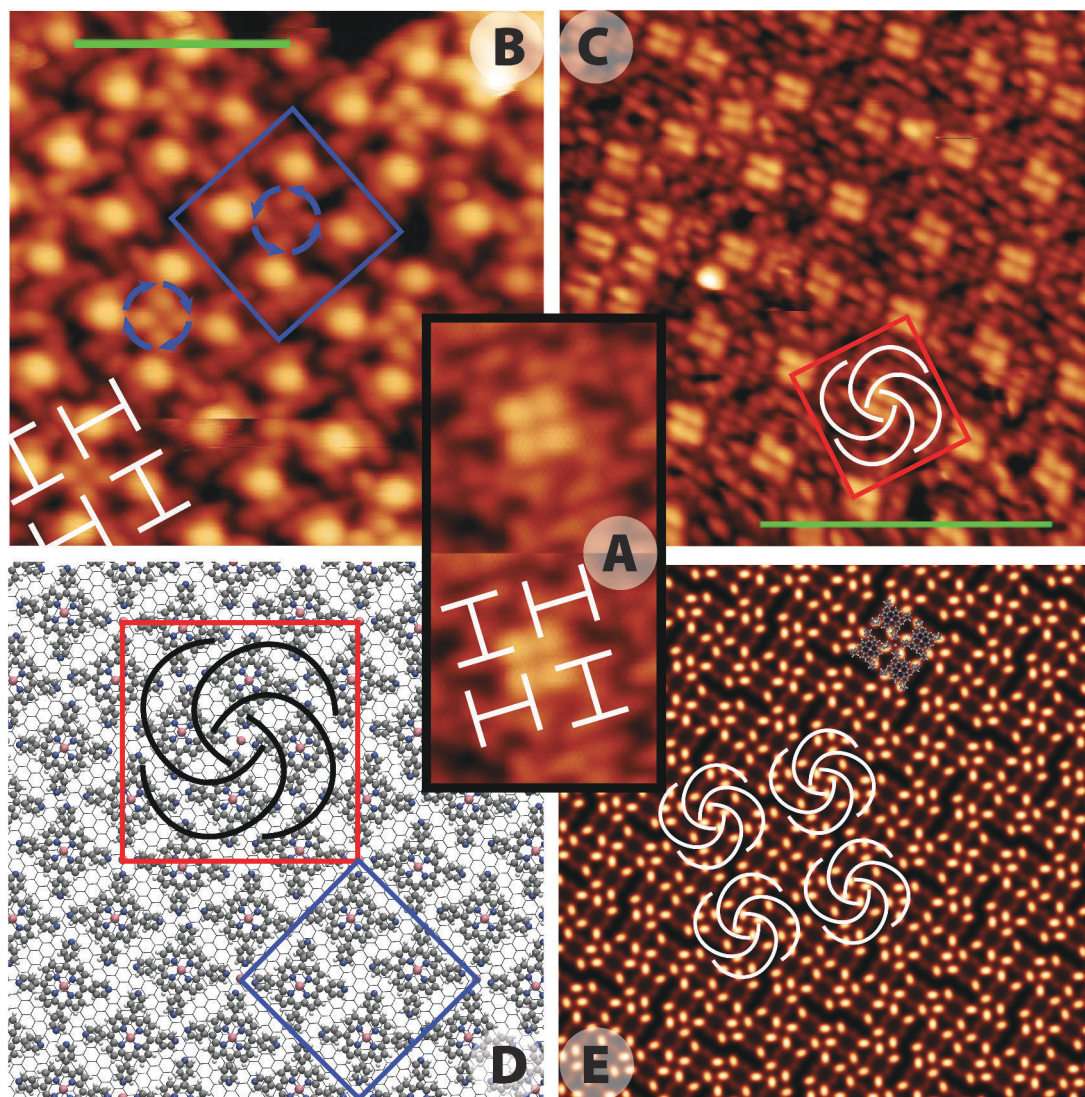


Figure 2.10: Experimental STM images and models for an unsaturated molecular layer: A) STM image of a single (CoTPyP)₄Co block acquired at $I = 60$ pA and $U_{bias} = +2.0$ V; the superimposed "H" shapes highlight the orientation of the molecules; B) STM image of a domain with a regular periodicity and a peripheral Co coverage $\theta_{Co}/\theta_{CoTPyP} = 0.25$ acquired at $I = 100$ pA and $U_{bias} = +2.0$ V, circular arrows indicate the different chirality of two adjacent (CoTPyP)₄Co blocks; blue cell indicates the apparent 2×2 periodicity (scale bar 4 nm); C) STM image of a different domain with the same periodicity and Co coverage of panel B) acquired at $I = 100$ pA and $U_{bias} = +1.4$ V; the superimposed "pinwheel" highlights the chiral structure (scale bar 10 nm); red cell indicates the effective $(2\sqrt{2} \times 2\sqrt{2})R45^\circ$ periodicity; D) Model of the periodic layer of panels B) and C), with the blue cell representing the apparent 2×2 periodicity and the red supercell representing the true $(2\sqrt{2} \times 2\sqrt{2})R45^\circ$ periodicity that takes into account the chiral structure; E) Topographic map at 3.0 Å above Co atoms for the model in D) obtained by considering a superposition of 3D gaussians with $\sigma = 0.5$ Å centered on the atomic sites of the model.

2.2. GEOMETRICAL STRUCTURE

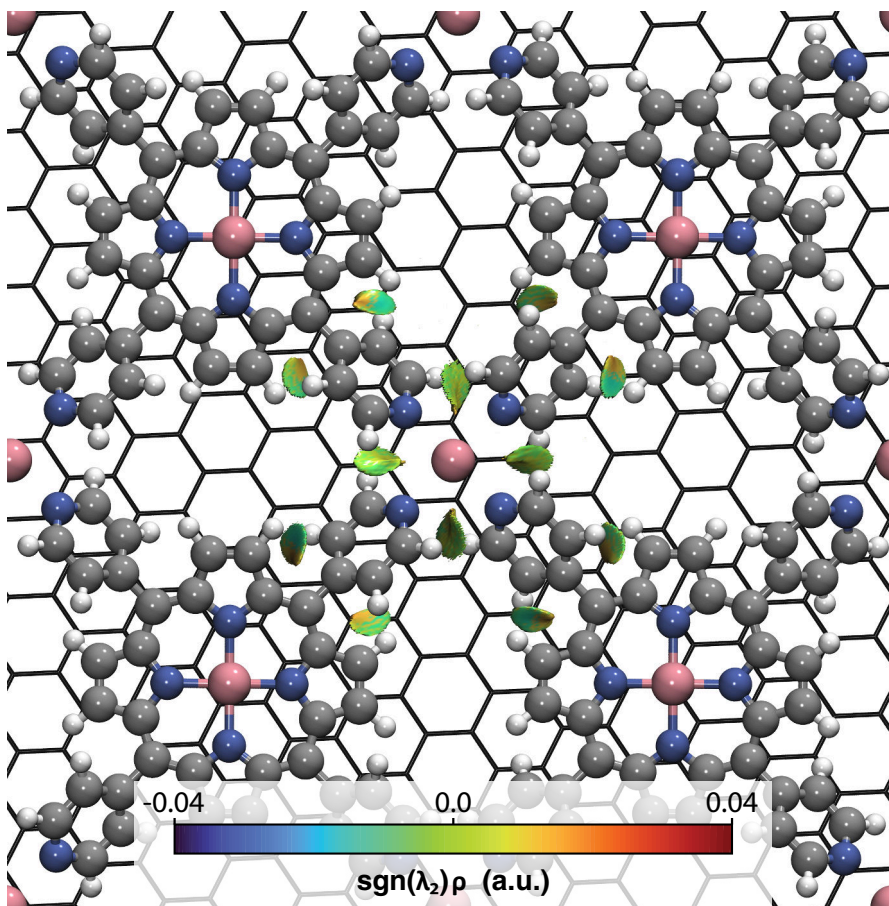


Figure 2.11: Non-covalent interacting regions responsible for the self-assembly of CoTPyP molecules. For clarity, the interacting regions involving just one pyridinic ring are shown. The RDG isosurfaces are plotted at 0.6 a.u. and colored according to the sign of the second eigenvalue of Laplacian of the electron density.

appear to be rotated in the same direction (fig. 2.11) and donate a specific chirality to the molecular assembly, which will be referred to as *minor chirality*.

At a Co coverage $\Theta = 0.25$, a regular arrangement of such blocks is visible, forming an almost square lattice with an apparent 2×2 periodicity (fig. 2.10 panel B).

Upon closer examination of this image, where the molecular orientation (the "H" shape) is visible, it becomes apparent that adjacent blocks exhibit opposite chirality. This leads to an increased actual periodicity of $(2\sqrt{2} \times 2\sqrt{2})R45^\circ$ (red cell in panel D). As a result, adjacent CoTPyPs from neighboring blocks share the same orientation, while inside the block, they are rotated alternatively by 90° , forming chains of "H H $\boxtimes$ $\boxtimes$ " oriented molecules.

This generates *larger* chiral features that are clearly visible in larger-scale STM images captured at $I = 100$ pA and a bias of +1.4 eV (Panel C). In this larger-scale image, the bright square features are formed by the four pyridinic rings bonding the peripheral Co atoms, while the Co atoms themselves are not visible at this bias. Careful examination reveals that the molecular ordering surrounding one new Co center every two results in the entire molecular domain exhibiting a specific chirality. To provide visual guidance, a white *pinwheel* is included.

Performing a full DFT calculation for such a large structure is computationally demanding. Therefore, to identify the origin of this chiral structure, an electron density distribution was simulated by considering the superposition of 3D Gaussian functions centered at the atomic sites (fig. 2.10, panel E). The atomic positions, along with lattice parameters, were derived from the STM image in panel B, assuming that the molecular conformation remains unaltered compared to the CoTPyP layer. The resulting map, obtained by slicing the simulated electron density at 3.0 Å above Co atoms, is in excellent agreement with the experimental image in panel C. It reveals that the "arms" of the pinwheels originate from the pyridinic rings not involved in bonding with the peripheral Co centers.

Another crucial factor explaining this distinctive shape is the rigid rotation of each block by approximately 7° anticlockwise. This rotation can be attributed to the interaction between molecules belonging to adjacent blocks, which is not mediated by the presence of a Co atom but rather by direct N-H hydrogen interactions between the pyridinic and iminic rings. This not only plays a fundamental role in aligning the pyridinic rings, as just explained, but also clarifies why not all peripheral Co centers, despite their equivalence except for the *minor chirality*, serve as centers for *pinwheel* features. This evidence underscores that the structural deformation is driven, on one hand, by the formation of blocks around a Co center facilitated by covalent interactions and, on the other hand, by the interaction between blocks driven by hydrogen bonds.

As the relative coverage of the deposited Co atoms increases, a further re-ordering phenomenon occurs, towards the creation of a MOF. It is worth noting that the location of Co atoms is not random; they preferentially bind laterally to the (CoTPyP)₄Co blocks rather than diagonally (i.e. with the same coordination of the peripheral Co in the center of the block). Small chains and domains exhibiting a local 1×1 ($\Theta = 1$) periodicity begin to form, suggesting a different arrangement of neighboring molecules (fig. 2.12, panel A). A closer inspection,

2.2. GEOMETRICAL STRUCTURE

guided by the H shapes, reveals that the "H H $\boxtimes$ $\boxtimes$ " chains transform into a "H $\boxtimes$ H $\boxtimes$ ". This transformation is only possible when each molecule in one block out of every two rotates by 90° . This rotation is fundamental to create a tetracoordinated site with the same pyridinic rotation. As a consequence, local chirality around the pyridinic Co atoms invert every adjacent site.

The dynamics of this process is not clear, and computationally expensive molecular dynamics simulations would be required for a detailed understanding. However, it can be speculated that the entire molecule does not rotate since this would require a high lattice distortion. A more plausible explanation is that only the pyridinic rings of selected molecules invert their rotation direction, causing also the macrocycle to invert its *saddle shape*.

Interestingly, on a larger scale (fig. 2.13), it becomes evident that saturation occurs primarily at the edges of the CoTPyP islands. This phenomenon can be attributed to the high mobility of Co atoms from the graphene sheet at the growth temperature of 500 K [54]. Additionally, at the island borders, CoTPyP molecules exhibit lower coordination and can rearrange more freely due to encountering lower energy barriers.

SATURATED CoTPyP-Co LAYER

At full peripheral metal loading (i.e. $\Theta = 1$) over wide domains, the deposited atoms as well as the molecular centers form an almost perfect square lattice with an apparent 1×1 periodicity. For this reason, it is common to find tens-of-nm wide fully saturated islands which have completely detached from the rest of the layer, such as the one presented in fig. 2.12, panel B. However, as just introduced, the local chirality around the pyridinic Co atoms invert every neighboring site, and therefore the global arrangement has a chessboard structure which can be described by an oblique lattice (panel C). The atomistic model in this case is affordable by full DFT calculations and has been optimized, giving unit cell with primitive vectors $a = 28.4 \text{ \AA}$, $b = 20.2 \text{ \AA}$, angle $\alpha = 44.9^\circ$, and with two inequivalent molecules rotated by 90° relative to each other (fig. 2.12, panel C). This results in the same molecular density on the surface. No relevant modifications of the individual molecular shape are found with respect to the monometallic case, apart from a small increase in the CoTPyP-GR distance from ≈ 3.8 to $\approx 4.0 \text{ \AA}$, accompanied by an increase of the pyridinic rotation angle to $\theta = 38.3 \pm 0.8^\circ$.

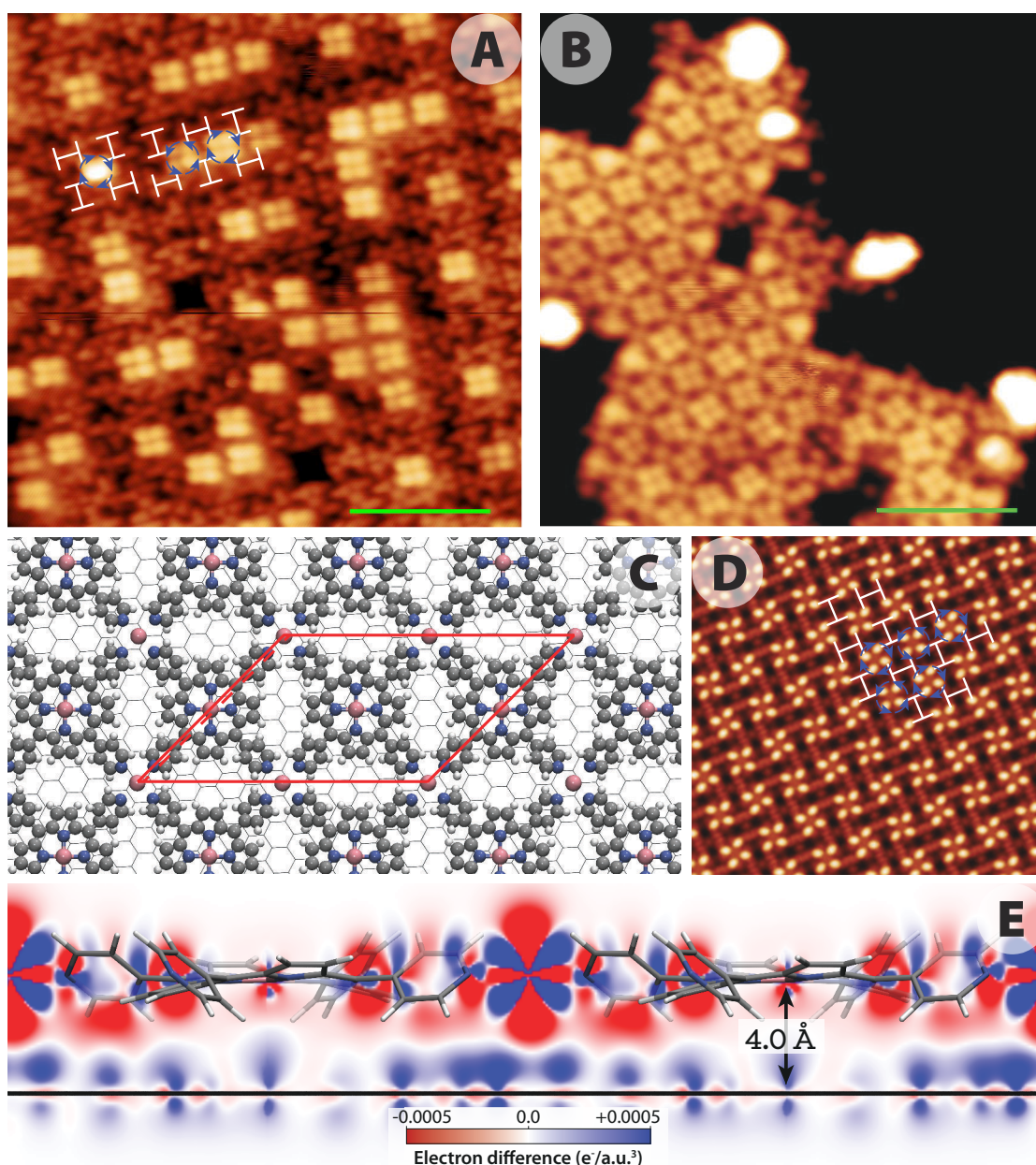


Figure 2.12: Bimetallic CoTPyP-Co molecular layer: A) Experimental STM image at partial peripheral Co coverage, acquired at $I = 60$ pA and $U_{bias} = +2.5$ V with superimposed H-model shapes highlighting the molecular orientation (scale bar 5 nm); B) Experimental STM image at full peripheral Co coverage ($\theta_{Co}/\theta_{CoTPyP} = 1$) acquired at $I = 50$ pA and $U_{bias} = +2.2$ V (scale bar 5 nm); C) Optimized DFT model (ball-and-stick rendering for the top view, with the supercell used; sticks only for the side view); D) Plot of the calculated electron density rearrangement due to the interaction between the molecular layer and GR on a plane perpendicular to GR and passing through the additional Co atoms, parallel to the short side of the supercell; E) Simulated STM image computed at constant height of 2.25 Å above Co atoms.

2.2. GEOMETRICAL STRUCTURE

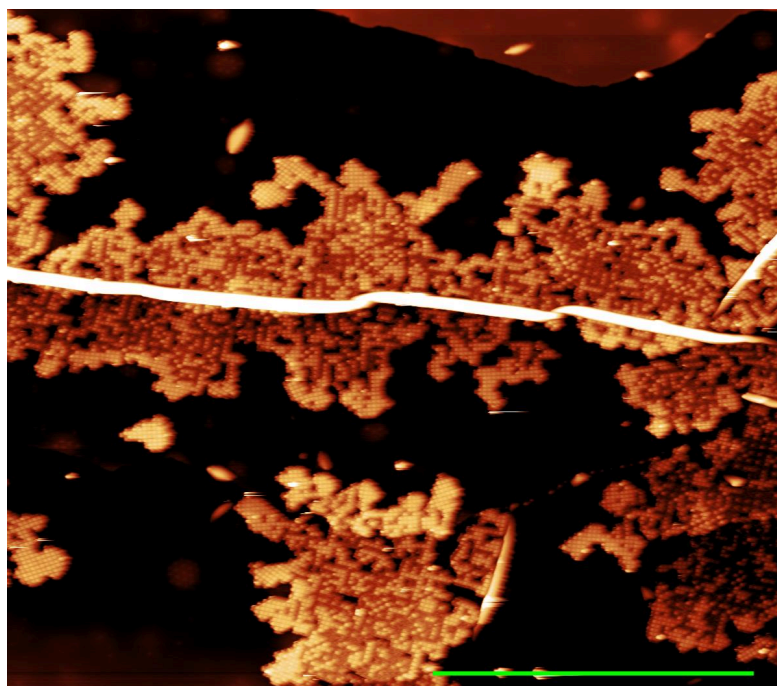


Figure 2.13: STM image of CoTPyPCo/Gr/Ir(111) at 1.2 ML of Co (with respect to CoTPyP unit cell). It can be observed that the molecular layer reaches saturation first at the borders of the islands. Image acquired at +2.2 V and 50 pA, scale bar = 100 nm.

Interestingly, the actual ordering of the evaporated Co atoms, at all loadings, is evidently not random, suggesting a long-range repulsive interaction between peripheral metal atoms that extends over distances greater than 3 nanometers. The exact nature of this interaction remains unclear. It could arise from geometrical hindrances caused by the rearrangement of molecules, or, more intriguingly, from a pyridyl-mediated antiferromagnetic coupling, as previously predicted by DFT in the case of the free-standing CoTPyPCo layer [55]. However, it is worth noting that in our calculations involving graphene, such a magnetic coupling is not observed. Indeed, when calculations are initialized with different combinations of starting magnetizations for the various Co atoms within the simulation cell, degenerate ground states result, with atomic magnetic moments determined by the initial sign choice.

Despite the 5% higher molecular-substrate distance, at full peripheral Co loading, a stronger interaction with the substrate is predicted with respect to the monometallic case, proved by a net charge transfer from the molecular layer to GR that, as we will see later on, can be quantified in $0.42 e^-$ per molecular layer unit. This is evident also in the charge density difference plot (fig. 2.12, panel

E), where a significant charge redistribution takes place between GR and the molecular layer, with major contributions coming from the peripheral metallic atoms and the pyridinic groups.

2.3 COMPREHENSIVE INVESTIGATION OF ELECTRONIC STRUCTURE

2.3.1 STS AND STM

From an experimental standpoint, a substantial collection of STS and STM images is available for all the systems discussed in the preceding sections. These images have been acquired at various bias voltages within the range of -2 V to +2 V, allowing for the exploration of both occupied and unoccupied states. To facilitate the comprehension of these images, where both electronic and structural properties are intertwined, they are compared with simulated ones.

CoTPyP/Gr/Ir(111) MONOLAYER

The central panel in fig. 2.14 reports an STS spectra for the monometallic CoTPyP layer. This dI/dV curve was acquired by fixing the position of the tip on top of a Co atom caged inside the molecule macrocycle and varying the applied bias. Hence, it resembles the LDoS on top of the metal atom, whose primary contribution can be attributed to vertical $3d_{z^2}$, $3d_{xz}$, and $3d_{yz}$ orbitals of Co. This curve exhibits a significant gap of about 2.7 eV. Furthermore, zooming in on the gap around the Fermi energy reveals the presence of low-intensity linear dispersive features, which are the signature of the graphene Dirac cones. These features are visible despite the considerable spatial separation between GR and the tip.

To compare with these spectra, the simulated DoS reported in fig. 2.15, projected onto all 3d states of Co, predicts a slightly larger gap (neglecting the in-plane Co orbitals that fall within this gap). Furthermore, by examining the orbital contribution to that DoS (see the colored flags in fig. 2.15), it is possible to attribute the Highest Occupied Molecular Orbital (HOMO) Co features to the $3d_{xz}$ and $3d_{yz}$ orbitals involved in the bond with surrounding N atoms, while the main unoccupied features correspond to the Co $3d_{z^2}$ states.

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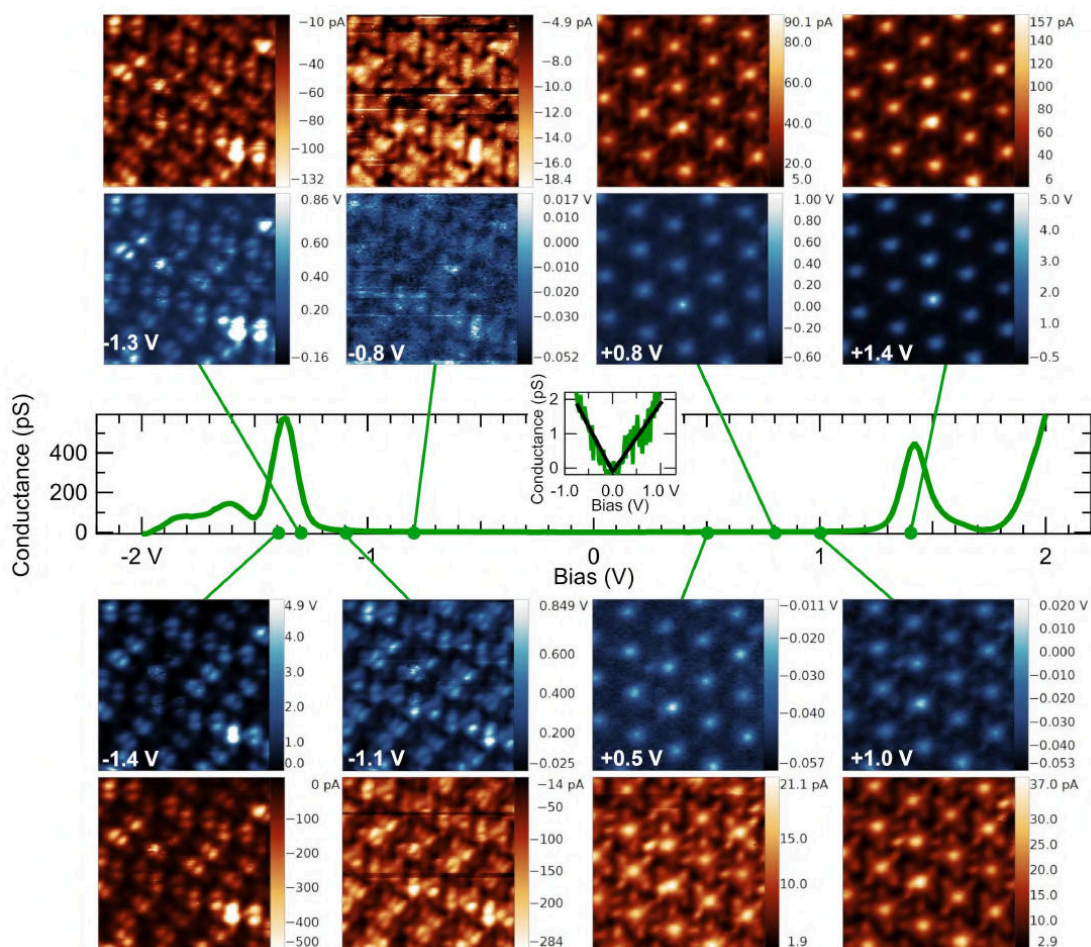


Figure 2.14: Experimental STS spectrum, dI/dV maps (blue palette), and simultaneously acquired current signal (red palette) of the CoTPyP/GR/Ir(111) monolayer at 77 K. In the inset, a zoom of the STS curve is reported. The STS spectrum is acquired on the cobalt with a starting setpoint of 2.0 V/0.2 nA. The dI/dV maps are collected with an initial setpoint of +1.4 V/300 pA, with the tip on top of the cobalt atom. The image size is 6 nm $\times$ 6 nm.

This observation aligns precisely with what is observed in the experimental images. Specifically, while the Lowest Unoccupied Molecular Orbital (LUMO) manifests as a highly luminous, well-localized spot at the center of the molecule, in the molecular HOMO, Co becomes less discernible, with the prominence of iminic features. Notably, when examining experimental images acquired at -1.3 V and -1.4 V, the electron charge distribution extends throughout the macrocycle. This distribution exhibits a two-fold symmetry stemming from the saddle shape of the macrocycle, wherein only iminic rings pointing upwards are visible as two *humps*. Additionally, the presence of a nodal plane, perpendicular to the

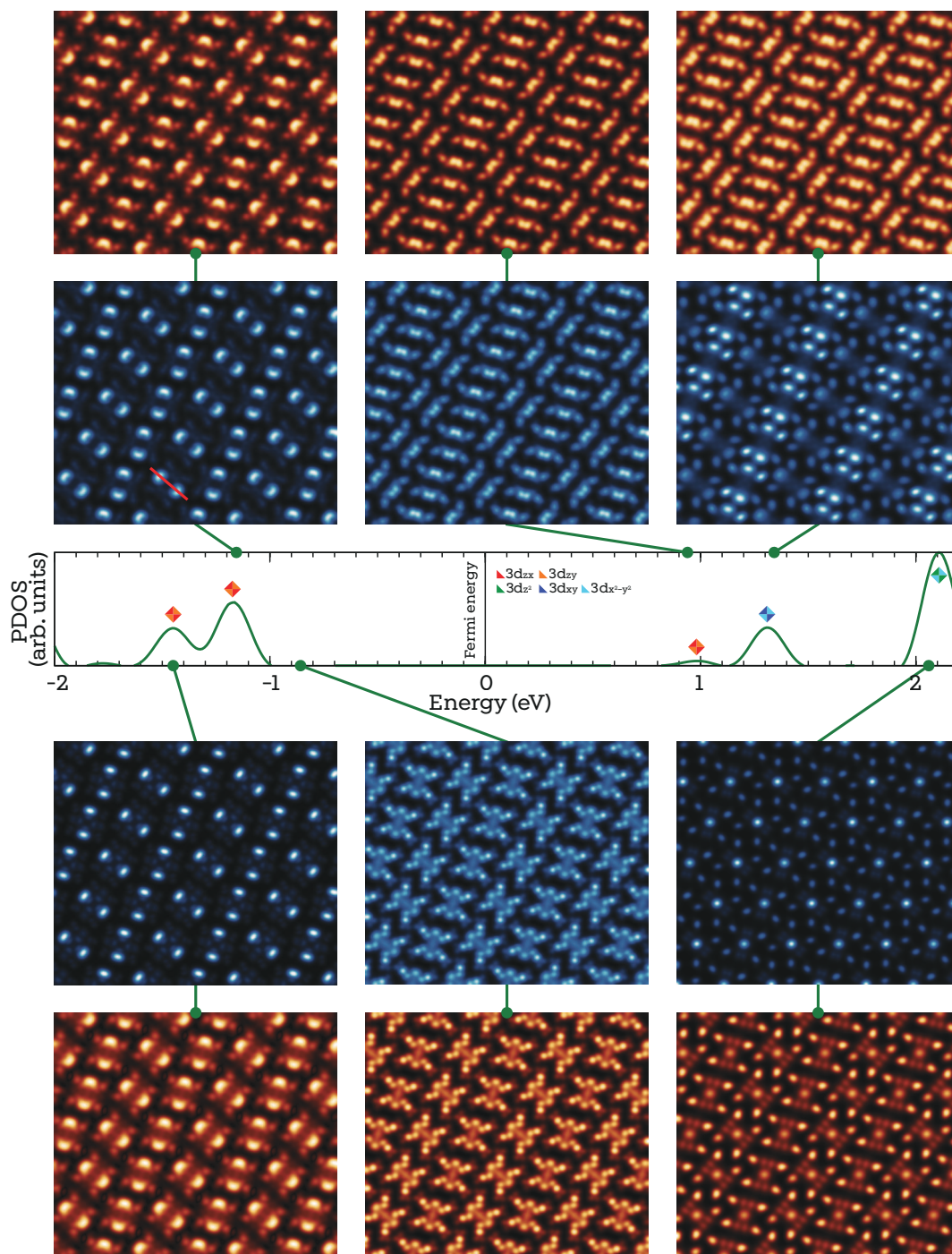


Figure 2.15: Simulated STS (blue palette) and STM (red palette) images of CoT-PyP layer on GR, with the corresponding DoS curves, projected on the 3d and 4s states of the two inequivalent Co species. The images are obtained at a distance between 2.5 and 3.0 Å above Co atoms. The colored squares, located at the peaks of DoS, represent the orbital contributions to these peaks.

2.3. COMPREHENSIVE INVESTIGATION OF ELECTRONIC STRUCTURE

graphene plane and passing through the two visible iminic rings, becomes apparent. This nodal plane is also observable in the simulated HOMO images (marked by a red line in fig. 2.15), albeit with less distinctiveness. Inside the gap are primarily evidenced topographic features of the molecule. Indeed, here, where the density of states is low, in experiments the tip is very close to the molecule, while in simulated images obtained at constant high, the contrast is enhanced. Molecules resembles a *butterfly* shape, where we can distinguish the contributions from the iminic rings pointing upwards, pyridin residues, and Co atoms.

When examining the LUMO region, can be observed distinct Co contributions in the PDoS spectrum at approximately +1.3 eV and +2.1 eV. At around +1.3 eV, the Co contribution primarily arises from in-plane $3d_{xy}$ and $3d_{x^2-y^2}$ orbitals, which play a crucial role in the formation of unoccupied orbitals involving nitrogen atoms. However, they do not prominently appear in STM images. Instead, at this energy level, can be primarily observed the two pirol rings oriented upwards and peripheral pyridinic rings in the STM images.

Moving to +2.1 eV, there is a distinct Co contribution originating from the $3d_{z^2}$ orbital. This results in a bright spot at the molecular center in the theoretical calculations. This observation aligns with experimental STM images where a similar contribution is clearly visible at lower energies in a broader range, between +1.5 and +2.0 eV.

CoTPyP-Co/Gr/Ir(111) MONOLAYER

In analogy to the experiments and simulations reported for the monometallic system, here are presented the results for the bimetallic one at full coverage. The central panel in fig. 2.16 displays two STS spectra acquired in an energy range spanning from -2.0 to 2.0 eV, each corresponding to a different Co specie. The red curve was acquired with the tip positioned directly above the cobalt atom embedded in the macrocycle, while the blue curve corresponds to the peripheral metal atom bonded to four adjacent pyridine rings. It is evident that the two Co species exhibit distinct features, which are also reflected in STM and STS maps.

These spectra can be directly compared with the PDoS for both metal species depicted in fig. 2.17. Again, a markedly different behavior is observed between the two metal sites.

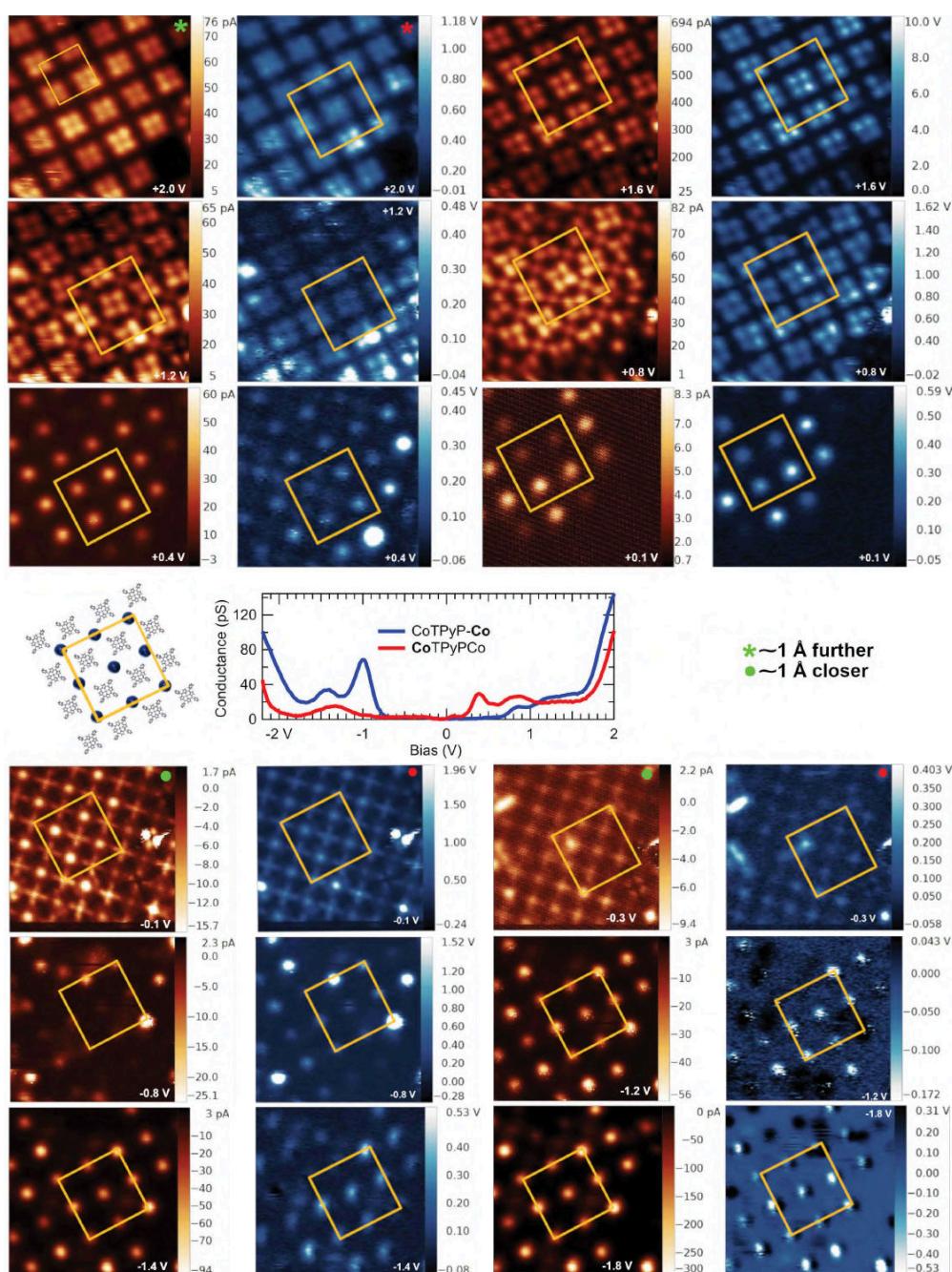


Figure 2.16: Experimental STS spectrum, dI/dV maps (blue palette) and simultaneously acquired current signal (red palette) of the CoTPyP-Co/GR/Ir(111) monolayer at 77 K. The STS spectrum was acquired with a starting setpoint of 2.0 V and 50 pA on top of the pyridinic cobalt. Blue STS spectrum was acquired on top of the external Co, while red spectrum was acquired on top of iminic Co. Asterisk and circle indicate images acquired with the tip 1 Å farther or closer with respect to the initial setpoint. Conventional unit cell is shown as yellow square. The map size is 6 nm $\times$ 6 nm.

2.3. COMPREHENSIVE INVESTIGATION OF ELECTRONIC STRUCTURE

Now, focusing on the iminic Co atom, in both the monometallic and bimetallic cases, there are observable differences in both the PDoS and STS spectra. Particularly, in the CoTPyP-Co layer, the Co PDoS appears to be shifted by approximately 0.7 eV toward higher binding energies. A similar shift is also noticeable in the experimental STS spectra when comparing the red curve in fig. 2.16 to the one in fig. 2.14. The newly emerged feature at +0.5 eV can be related to the +1.4 eV feature for CoTPyP and the old feature at -1.4 eV may now be associated with the new peak, which likely lies below -2.0 eV.

These observations manifest in the STM and STS maps as well. Specifically, the *humps* related to the upward-pointing pyrroles are no longer visible experimentally, although they are evident in the simulated images at lower energies. Therefore, it is reasonable to assume that they fall outside the experimental energy range considered. On the other hand, concerning unoccupied features, the bright spots with a spherical distribution attributed to cobalt $3d_{z^2}$ orbitals are experimentally visible closer to the Fermi energy, consistent with computed PDoS shift. These features are no longer visible in the simulated images, even though they remain present in the PDoS.

This behavior can be attributed to the fact that the peripheral Co atoms are positioned 0.2 Å higher than the central ones. Consequently, it is more likely for the peripheral contributions to be discernible, despite having smaller PDoS contributions, in particular since simulated images were obtained at constant high.

Due to this observation in both experimental and simulated images acquired above the Fermi level, the main feature that can be observed is the presence of square shapes made by four distinct bright spots. These bright spots are attributed to the four pyridinic rings bonding a peripheral Co atom, which appears as a dark depression at the center of the square. Interestingly, these squares appear to be alternately rotated clockwise and counterclockwise by a small angle. This rotation is related to the different chirality around those metallic centers due to the opposite rotation of pyridinic rings in the nearest squares.

On the other hand, below the Fermi energy, a much more intense contribution from these cobalts is visible. This is due to both a higher density of states contribution and a lower contribution coming from the pyridinic rings.

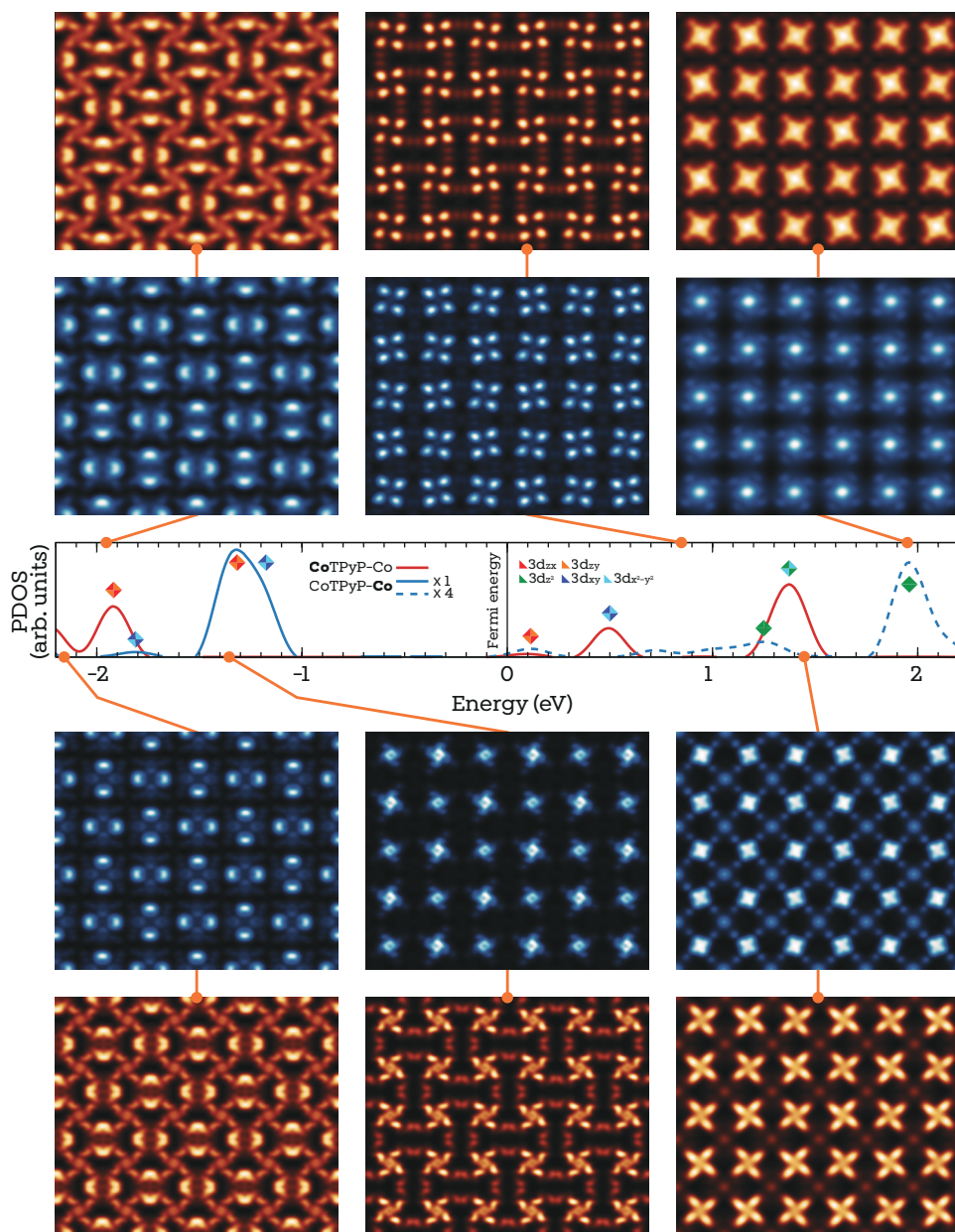


Figure 2.17: Simulated STS (blue palette) and STM (red palette) images of CoTPyP-Co MOF on GR, with the corresponding DoS curves, projected on the 3d and 4s states of the two inequivalent Co species. The images are obtained at a distance between 2.5 and 3.0 Å above Co atoms. The colored squares, located at the peaks of DoS, represent the orbital contributions to these peaks.

2.3.2 CORE LEVEL SHIFT

The study of CLS, which refers to how the binding energy of a core level changes, is a powerful tool for investigating the chemical environment of a specific atom. Indeed, core level binding energies are highly sensitive to the local coordination and chemical surroundings of the atom in question.

N 1s CLS

The analysis of nitrogen core levels is particularly interesting in this context because their changes during the bimetallation process can provide insights into the bonding of the additional metal atoms.

In our systems, two inequivalent nitrogen species are present. One is the iminic nitrogen within the molecular macrocycle, which maintains a well-defined and unchanging chemical environment, at least under the experimental conditions of interest. The other is the pyridinic nitrogen within the peripheral residues, that undergoes a coordination change from mono- to bimetallic system.

The calculation of CLS for the CoTPyP layer is quite difficult. Indeed, the computed total energy with the full core hole results to be very sensitive to the selected atom. Indeed, even for equivalent atoms different core levels are predicted. The calculations seem to fall in different minima configurations with different magnetic configurations. This is probably due to the use of Hubbard correction that can lead the system to fall in different local minima. Choosing the configurations corresponding to minimum energy for both iminic and pyridinic nitrogens, a 0.39 eV CLS is predicted. Here the pyridinic component has lower binding energy. On the other hand, from the deconvolution of experimental X-ray Photoelectron Spectroscopy (XPS) spectra (fig. 2.18) with two components (in order to take into account for the two N species) a 0.28 eV CLS is obtained, with the iminic contribution centered at 399.10 eV and the pyridinic one at 398.82 eV. This component attribution is based on previous literature [56], but is clearly in disagreement with the ordering coming from simulations.

The CLS was also computed for the single molecule on graphene. In this case, the total energies remain consistent when different N atoms were selected, resulting in a CLS of 0.28 eV. Furthermore, the same binding energy ordering as suggested in the literature was predicted. Since no other significant electronic differences were found comparing that system with the CoTPyP layer, this value

can be reasonably considered as a good approximation also for the CLS of the CoTPyP layer. In this case, there is a perfect agreement with experimental results.

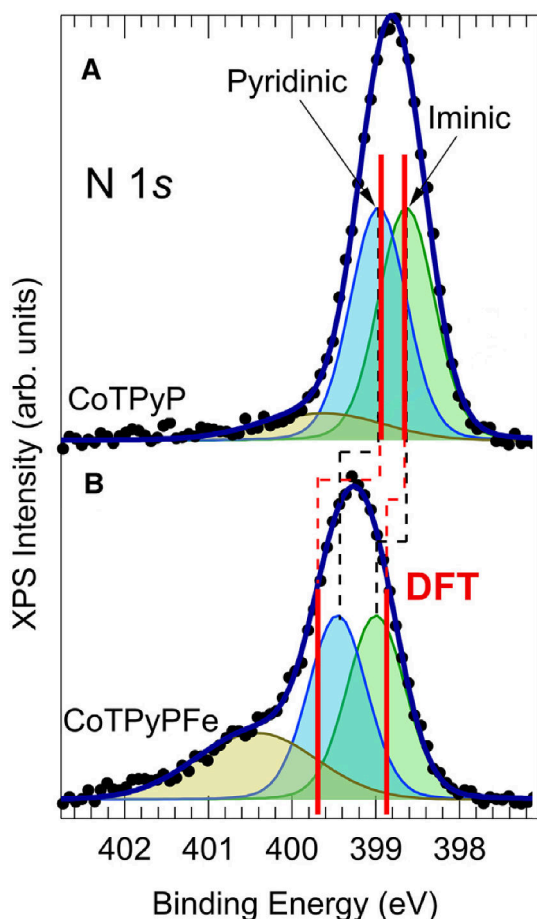


Figure 2.18: XPS spectra for N 1s core level. Experimental data with their deconvolution. The red lines indicate the DFT prediction for the CLS of two N species. The DFT result superposed on the CoTPyP spectra was obtained for the single molecule on graphene.

chemical shift of +210 meV is observed for the peak associated with the iminic N species. This indicates that the electronic configuration of the macrocycle is also affected upon the formation of the MOF, leading to a shift of the energy levels.

In order to align with experimental measurements conducted on a bimetallic system, where additional iron atoms were deposited onto the system, the CLS was also computed for the bimetallic CoTPyP-Fe layer. In this case, the atomic positions were constrained to the relaxed positions obtained for the CoTPyP-Co system, with only an exchange of peripheral atoms being made. Additionally, also for the Fe atoms, a Hubbard correction was introduced with $U = 6.4$ eV, following literature [57].

This calculation did not suffer from the problems encountered in the CoTPyP case and resulted in a CLS of 0.82 eV. Similar to what was obtained for the single molecule, the iminic component is predicted to have a lower binding energy than the pyridinic one. This aligns well with the experimental XPS spectra, although a smaller CLS of 0.40 eV is observed experimentally. In the experimental data, the contribution attributed to the pyridinic N undergoes a chemical shift of +330 meV due to direct binding with the iron atom. Additionally, a significant

Co 2p_{3/2} CLS

Cobalt core level spectra can provide information about the equivalence of the Co species in the system and their oxidation states. Specifically the 2p_{3/2} core level is considered, which exhibits a complex structure due to the coupling in the photoemission process between the ionized 2p core level and the high-spin valence electrons. Since obtaining the multiplet splitting would be challenging at the DFT level, here the focus is on reporting the experimental results that are relevant for the subsequent analysis.

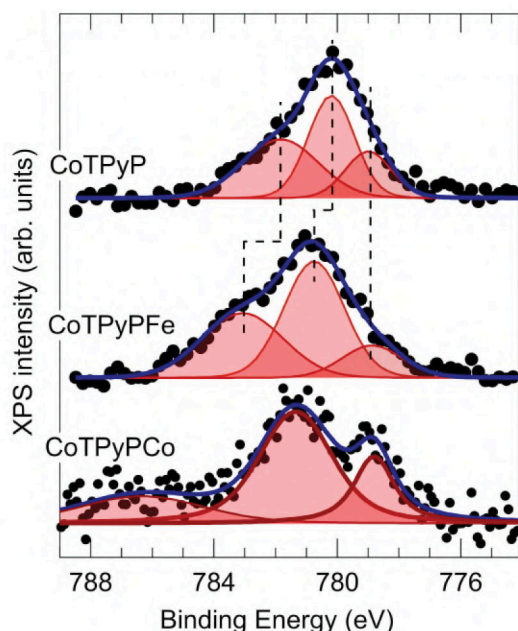


Figure 2.19: XPS spectra for Co 2p_{3/2} core level for the monometallic CoTPyP system and the bimetallic CoTPyP-Co and CoTPyP-Fe systems.

other (imino) contributions toward lower binding energies, also present in this case, indicates a change occurring at valence levels. One possibility is the change in the oxidation state of the Co atom caged in the macrocycle to +3 value.

In summary, both N 1s and Co 2p_{3/2} core level spectra indicate that the bimetallic system is characterized by two inequivalent Co and N species, and the bimetalation process also leads to a change in the electronic configuration

For the monometallic CoTPyP spectrum, three major components can be identified (fig. 2.19). The two peaks at higher binding energies (782.2 and 780.6 eV) are associated with the Co multiplet splitting, while the third peak (at 779.4 eV) corresponds to the Gunnarsson-Schönhammer relaxation process involving charge transfer to unoccupied Co molecular orbitals.

In the CoTPyP-Fe monolayer, a shift of +0.3 eV and +0.6 eV is observed for the two peaks at higher binding energies, which follows what was observed for the N 1s core level.

In the CoTPyP-Co system, a peak at 778.8 eV grows and can be attributed to the presence of peripheral metal atoms, specifically a Co specie in the +1 oxidation state. The shift of the

of the macrocycle.

2.3.3 NEXAFS

NEXAFS is a powerful technique sensitive to the chemical environment of a selected element, since it indirectly probes the unoccupied molecular orbitals of the system just above Fermi energy. Here are compared simulated and experimental NEXAFS spectra for the N K-edge of both monometallic CoTPyP layer and bimetallic CoTPyP-Fe. This comparison is useful to confirm the molecular adsorption geometry and can prove the binding of a single metal specie to the pyridinic groups. In the computation of these spectra, for p polarization, the electric field was considered along the z-axis. For s polarization, it was taken in both the x and y directions, and the resulting spectrum was the average of the two. This choice was made to replicate the experimental conditions. Indeed, NEXAFS inherently provides averaged information over a large sample area (on the micrometer scale), encompassing different domains with various molecular orientations. Furthermore the spectra were aligned on the absolute photon energy scale by matching the experimental N K-edge.

CoTPyP LAYER

In fig. 2.20, the simulated NEXAFS spectra for the N K-edge are presented for both polarizations, corresponding to the monometallic CoTPyP layer on GR. Additionally, the experimental spectra are included for comparison. These calculations were obtained by computing the transition amplitudes with the Half Core Hole (HCH) method on the CoTPyP monolayer system. During the plotting process, the spectra acquired with the HCH on the two N species are shifted accordingly to their relative CLS. The CLS obtained for the single molecule was used, in accordance with what was discussed in the previous section.

The simulated spectra confirm the attribution of peaks related to the two N species as determined in the experimental deconvolution, based on previous literature². Focusing on the iminic contributions (in green), can be observed a

²In the experimental peak deconvolution and attribution a *building block* approach was used. Fe(II)-tetra phenyl porphyrin (FeTPP) and pyridine molecules, previously studied in literature [14, 15], were used as spectroscopic reference, since they present exclusively the iminic or the pyridinic nitrogen species, respectively.

2.3. COMPREHENSIVE INVESTIGATION OF ELECTRONIC STRUCTURE

complete dichroic character of the peaks in the region between 400 and 403 eV. These peaks, which are present only in p polarization, originate from the p_z orbitals of the iminic nitrogens, and as such, have a vanishing in-plane component. This observation would suggest that the macrocycle is completely flat. However, when examining the main feature at 398.5 eV, it is present in both polarizations, albeit with reduced intensity in s polarization. This suggests instead that, due to the saddle shape of the macrocycle, the π^* molecular orbitals originating from p_x and p_y N orbitals are not perfectly parallel to graphene.

On the other hand, when looking at the pyridinic component (in blue), all associated peaks exhibit partial dichroism. This can be attributed to a π^* molecular orbital that is delocalized on the pyridinic ring. Since the latter is not flat, this orbital has both vertical and in-plane components. Therefore, from an experimental perspective, a rotation of pyridinic rings with an angle of $36 \pm 4^\circ$ is predicted. This value is in good agreement with the angle of 38° obtained from simulations through a relaxation calculation.

Therefore, this picture confirms the molecular adsorption geometry described in a previous section, where the macrocycle has a *saddle shape* and the pyridinic rings are tilted with respect to the graphene plane.

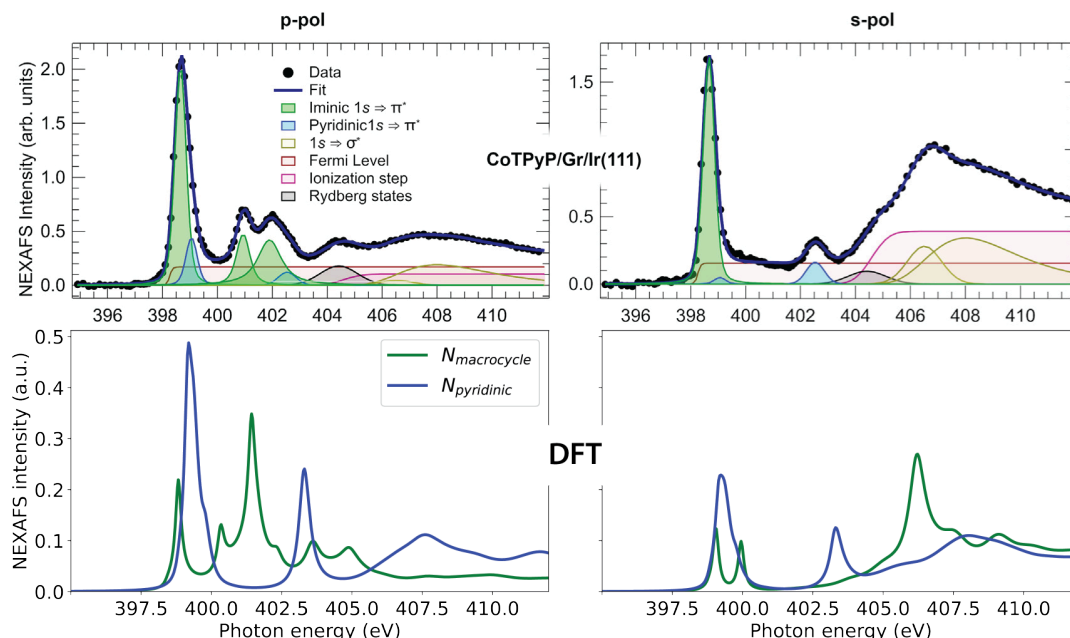


Figure 2.20: Experimental and simulated NEXAFS spectra for N K-edge in both p and s polarizations for the monometallic CoTPyP layer on GR.

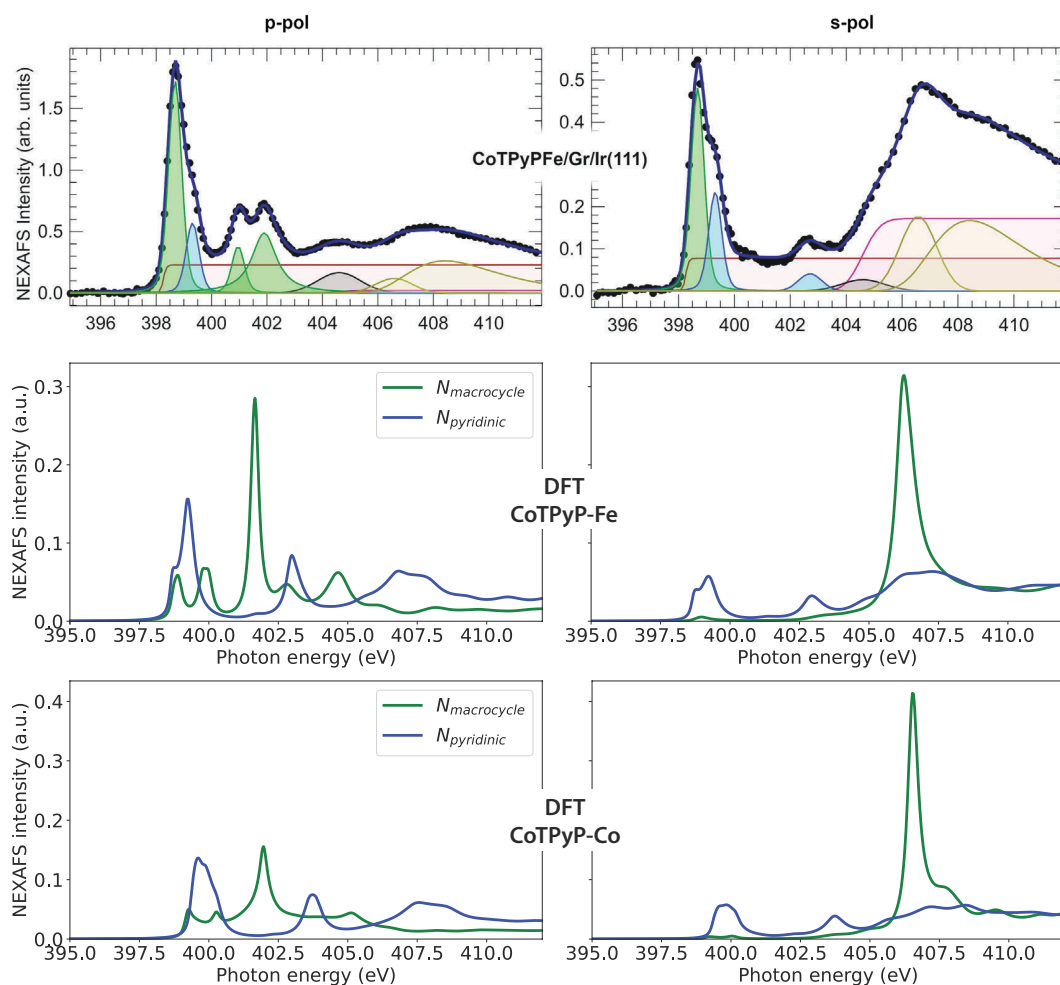


Figure 2.21: Experimental and simulated NEXAFS spectra for N K-edge in both p and s polarizations for the bimetallic CoTPyP-Fe layers on GR and simulated one for the CoTPyP-Co layer.

CoTPyP-Fe AND CoTPyP-Co LAYERS

In fig. 2.21, the simulated NEXAFS spectra for the two bimetallic CoTPyP-Co and CoTPyP-Fe layers on GR, along with the experimental spectra for the CoTPyP-Fe MOF, are presented. All of these spectra exhibit a totally similar dichroic behavior for all the resonances. This confirms that the molecular geometry is not significantly affected by the presence of additional metal atoms at the periphery. The main difference between these spectra is seen in the main peak, which appears to be clearly split into two components. This is directly related to the increased CLS of the two N species in the bimetallic system, which results in a different photon energy needed to excite the two species. Furthermore, when

2.3. COMPREHENSIVE INVESTIGATION OF ELECTRONIC STRUCTURE

comparing the ab initio results for the two systems, it is evident that the change of the metal atom at the periphery does not significantly affect the spectra, which maintain a similar shape and intensity.

These observations effectively rule out any hypothesis of the existence of domains in the experimental samples where a different and more exotic adsorption geometry is present for both mono and bimetallic systems.

2.3.4 WORK FUNCTION

An important property for characterizing the electronic structure of materials is the Work Function (WF). The WF (ϕ) is defined as the minimum energy required to extract one electron from the system.

For slab systems like the one under study here, the WF can be divided into two contributions: one originating from the bulk and the other from the surface. The surface contribution can be described using a "jellium model" as arising from the "spilling out" of electrons from the bulk into the vacuum region, creating an electrostatic dipole layer at the surface. Only this surface contribution is sensitive to the charge redistribution caused by the adsorption of atoms or molecules on the surface [58, 59]. A change in the WF can influence surface reactivity due to a different surface dipole [60].

This quantity can be computed within the DFT framework as the difference between the Electrostatic Potential (EP) in vacuum, sufficiently above the molecular layer, and the Fermi level of the system. Specifically, the average EP on planes perpendicular to the z-axis was considered. Table 2.1 presents the computed and experimental values for the different systems under study. The mean EP for the monometallic CoTPyP and bimetallic CoTPyP-Co systems is depicted in fig. 2.22.

For bare GR on Ir(111), a ϕ value of 4.4 eV was computed, aligning with the experimental value of 4.65 eV [61]. This value slightly reduces to 4.2 eV for the freestanding GR layer, attributable to the absence of the underlying Ir(111) surface, which has a higher work function and induces a small charge transfer from GR.

Notably, the WF of the system remains relatively stable upon CoTPyP molecule adsorption. The lack of a significant change is due to the physisorption nature of the molecule on the surface, where no charge transfer occurs between the molecule and the substrate, and the absence of a permanent dipole in TPyP

	Work Function	
	DFT	EXP
GR/Ir(111)	4.4 eV	4.65 eV [61]
Ir(111)		5.78 eV [62]
GR	4.2 eV	
CoTPyP/GR (single molecule)	4.3 eV	
CoTPyP/GR (molecular layer)	4.3 eV	4.5 eV
CoTPyP-Co/GR	3.1 eV	3.6 eV

Table 2.1: Computed and experimental values for the WF of the different systems under study.

molecules. Consequently, no substantial alteration is expected upon the formation of the monometallic CoTPyP layer.

In contrast, the formation of the bimetallic CoTPyP-Co layer causes a considerable reduction in the system's WF. This reduction is directly related to the observed charge transfer to the GR. Both theoretical and experimental results confirm a significant reduction of about 1 eV ($\Delta\phi_{\text{th}} = 1.2$ eV, $\Delta\phi_{\text{exp}} = 0.8$ eV). This suggests that even a minute quantity of peripheral Co atoms contributes to a profound alteration in the surface's electronic structure, aligning with the previously presented results.

This charge transfer responsible for the reduction in the WF is also reflected in the PDoS of GR reported in fig. 2.23. Indeed, while the Dirac cone is located at the Fermi energy for the monometallic CoTPyP layer, as for freestanding GR, it is shifted by about 0.5 eV towards lower energies for the bimetallic CoTPyP-Co MOF. The amount of electrons transferred from the molecular layer to GR in this case could not be directly computed from the analysis of Löwdin charges. Indeed, the charge transfer is too small and falls well beyond the spilling parameter. However, it can be estimated by integrating the PDoS of GR in the energy range between the Dirac point and the Fermi energy. In doing that the DoS of GR can be decently approximated by a linear function of the energy in the ± 1 eV range, i.e., $D(E) = D_0|E|$, with $D_0=0.09$ eV² per GR unit cell[63]. By integration the number of transferred electrons is $N = \pm D_0 \Delta E_F^2 / 2$ leading to 0.42 e⁻ transferred from each molecular layer unit to the substrate.

2.3. COMPREHENSIVE INVESTIGATION OF ELECTRONIC STRUCTURE

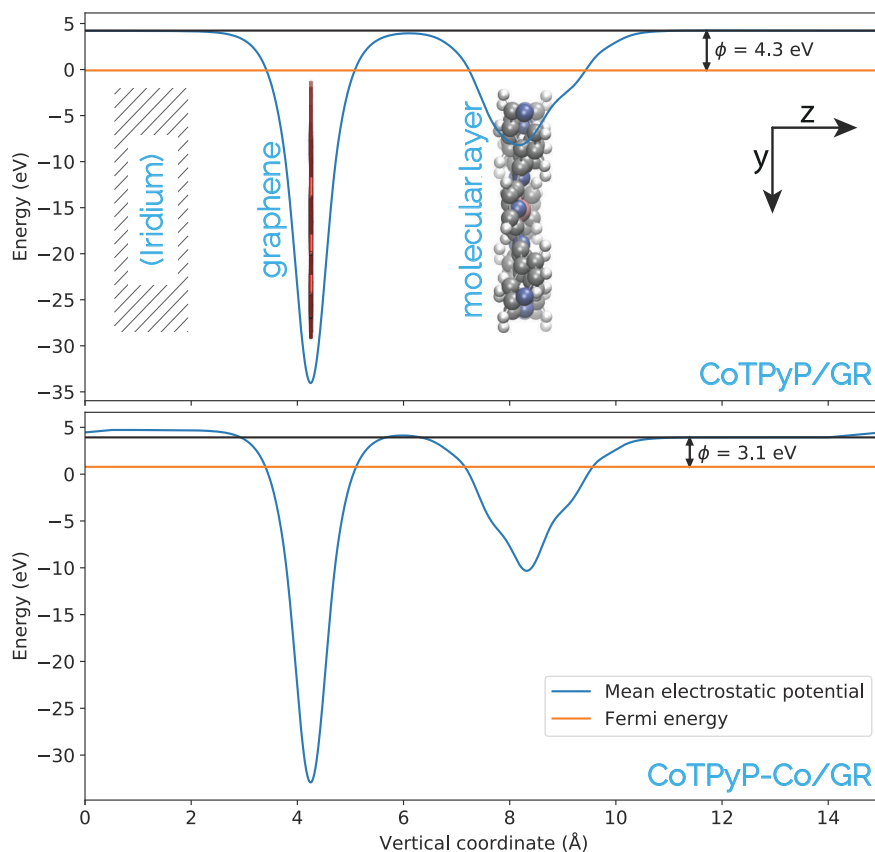


Figure 2.22: Computed electrostatic potential profile of both monometallic CoTPyP and bimetallic CoTPyP-Co molecular layers from which the work function has been extracted. The non-zero slope of the mean electrostatic potential at the cell edges is due to the application of a dipole correction.

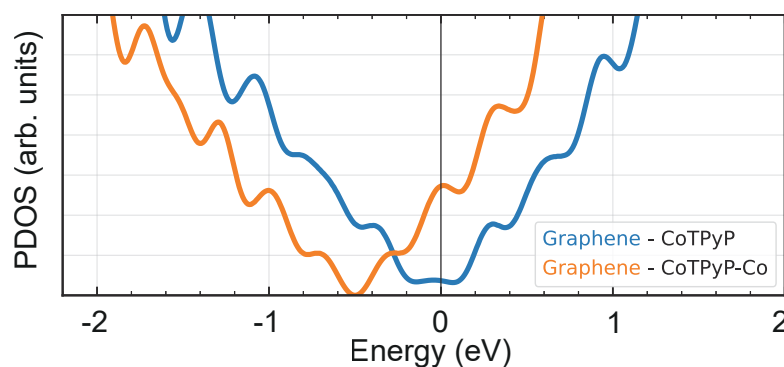


Figure 2.23: PDOS on graphene C atoms for both monometallic CoTPyP and bimetallic CoTPyP-Co molecular layers. The Fermi level is set to zero.

2.3.5 TOWARDS REACTIVITY: CO ATOMS

To delve into the investigation of the reactivity of TPyP layers, this section will focus on the Co atoms, as they serve as the active sites for the catalytic activity of the system. The electronic characteristics of these Co atoms and the nature of their bonding with the surrounding nitrogens will be deeply investigated since they are the key factors in determining the reactivity of the system.

ORBITAL OCCUPATION AND OXIDATION STATE

The cobalt atom possesses an electronic configuration of $[Ar]3d^74s^2$ with nine valence electrons. However, Co is commonly found in chemical compounds with Oxidation State (OS) of +2 or +3, resulting in the loss of electrons in favor of other ligands.

This is the case of metal atoms caged inside TPyP molecules. When they are not metallated, the macrocycle is saturated by two hydrogens. However, upon metallation, these hydrogens are substituted by a metal atom that assumes a +2 oxidation state [30, 64]. This electron donation from the Transition Metal (TM) (Mn, Fe, Co, ...) leads to an increase in the binding energy of the 3d states compared to 4s, causing a depletion of the latter.

This effect is evident looking at the Löwdin charges in fig. 2.24, where the orbital occupations for all Co atoms in both mono and bimetallic systems are reported schematically. Indeed, in all the cases, the occupation of 4s orbitals is drastically reduced.

Focusing on the iminic Co, which have the same chemical environment in both monometallic and bimetallic systems, their occupation of 3d orbitals is identical in both systems. The only difference lies in the inverse occupation of in-plane orbitals. However, this is not a physical distinction but rather a result of the molecule's different orientation with respect to the Cartesian axis orientation. In fact, the $d_{x^2-y^2}$ and d_{xy} orbitals are equivalent upon a rotation of 45° around the z-axis.

This observation confirms that iminic centers are not significantly affected by peripheral changes, such as molecular rearrangement and the addition of metallic atoms.

2.3. COMPREHENSIVE INVESTIGATION OF ELECTRONIC STRUCTURE

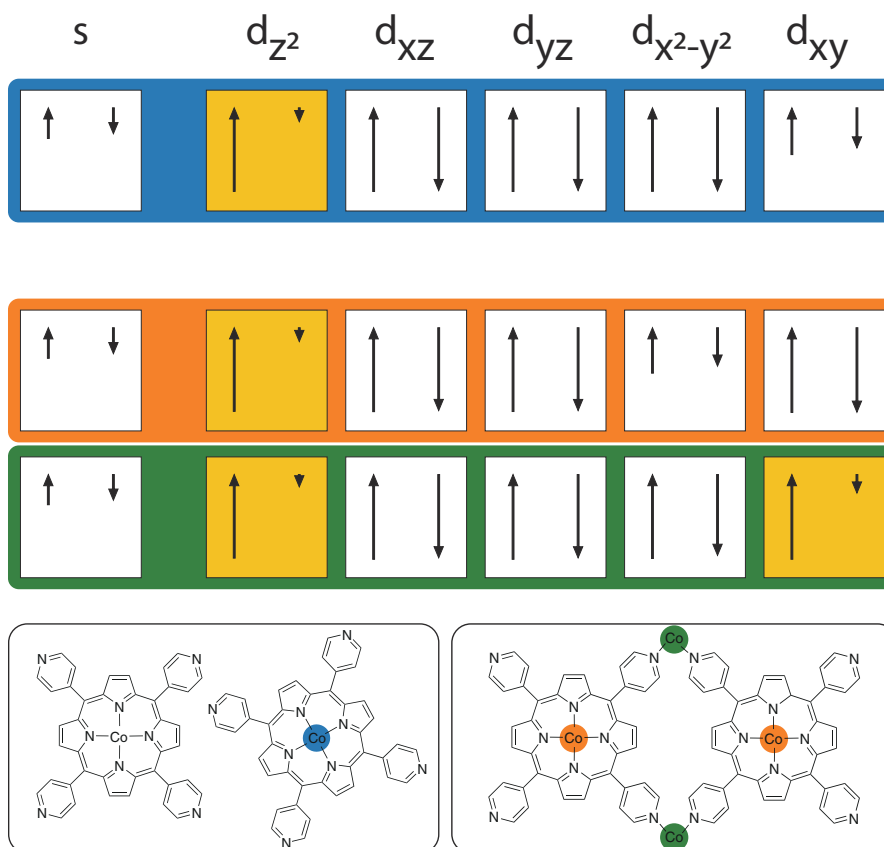


Figure 2.24: Schematic representation of orbital occupation for iminic Co atom in monometallic layer and for both iminic and pyridinic metal species in the CoTPyP-Co MOF. With yellow background are highlighted the orbitals that give the major contribution to the magnetic moment.

As shown in table 2.2, Co atoms lose fewer than 1 electron³, which would result in an oxidation state of +1 if the oxidation number is solely based on physical atomic ionization. However, as highlighted by Raebiger and colleagues [65], when charge transfer occurs to or from a TM, a negative-feedback charge regulation takes place that tends to maintain the local charge constant.

Therefore, for the attribution of the oxidation states, following the method proposed by Sit et al. [66], only the number of d-orbitals with full occupancy (i.e., occupation number ≈ 1) is considered, while the others are associated with the back-donation process. The OS is then determined by the difference between

³This charge transfer is computed as the difference between the number of valence electrons and the sum of Löwdin charges. However, the latter are computed by projection onto the atomic orbitals, that do not necessarily form a complete base set. Therefore, a fraction of the charge loss ($\sim 10/15\%$) has to be attributed to the basis set incompleteness.

	Charge	Magnetization	Oxidation state	
			DFT	EXP
CoTPyP	$8.16 e^-$	$1.1 \mu_B$	+2	+2
CoTPyP-Co	$8.15 e^-$	$1.1 \mu_B$	+2	+1-+3
CoTPyP-Co	$8.36 e^-$	$2.0 \mu_B$	+1	+1-+3

Table 2.2: Summary of the electronic properties of Co species in the monometallic and bimetallic systems.

this quantity and the number of valence electrons of the Co atom. In this way, for the iminic Co atoms, a +2 OS is predicted.

Peripheral Co atoms, on the other hand, exhibit a different electronic configuration. The number of valence electrons is only slightly higher than that of the other Co species, but they have a distinct occupation of one in-plane orbital. This results in a double magnetic moment and a reduction of the OS to +1.

The differing electronic configurations that result in distinct oxidation states (OS) can potentially lead to varying reactivities for the two Co species, making them active in different chemical reactions.

SHIFT OF VALENCE LEVELS

In the top panel of fig. 2.25, the total PDoS for all Co atoms in the monometallic and bimetallic systems are compared. Can be observed that the addition of a peripheral Co atom leads to a shift in the valence levels of the iminic Co. The shape of the PDoS curves remains almost identical, except for a consistent rigid shift of the energy levels by 0.6-0.7 eV towards higher binding energies. This observation, coupled with the unaffected electronic configuration of the iminic Co atom, allows to dismiss the experimental hypothesis of a change in oxidation state as the cause of the observed shift in the XPS spectra. Instead, this shift must be attributed to a change in the binding energy of the valence levels.

A compatible shift was also experimentally observed through Ultraviolet Photoelectron Spectroscopy (UPS), as shown in fig. 2.26. Comparing the peaks for the two systems, a consistent rigid shift of 0.7 eV can be identified. This shift is also corroborated by both experimental and DFT-simulated STM images, where all the features are observed to shift accordingly.

Furthermore, in the MOF UPS spectrum, a new contribution arises at approximately 1 eV below the Fermi energy. This new peak can be attributed to the presence of the new peripheral Co species, as it is absent in the monometallic

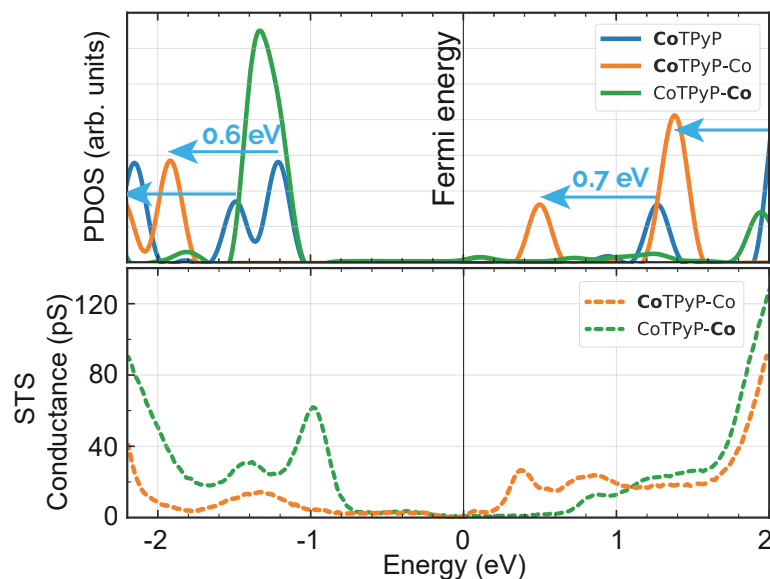


Figure 2.25: PDoS on the iminic Co atom for both monometallic and bimetallic systems and on peripheral Co for the CoTPyP MOF (top panel) together with the experimental STS spectra acquired with the tip on top of the two Co species in the bimetallic layer (bottom panel).

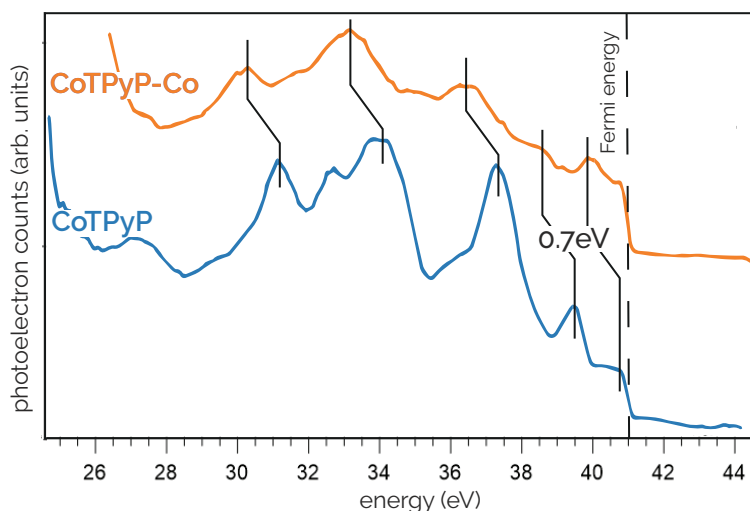


Figure 2.26: Experimental UPS spectra for both monometallic and bimetallic layers acquired using He II emission line at 40.8 eV. For better clarity, the spectra are vertically shifted.

system. Indeed, when examining the STS spectra in fig. 2.25, it is evident that the peripheral Co atom exhibits this new contribution. Additionally, the PDoS computed for this atom reveals that it has a different shape compared to the iminic metal and makes a significant contribution to the DoS just below -1 eV.

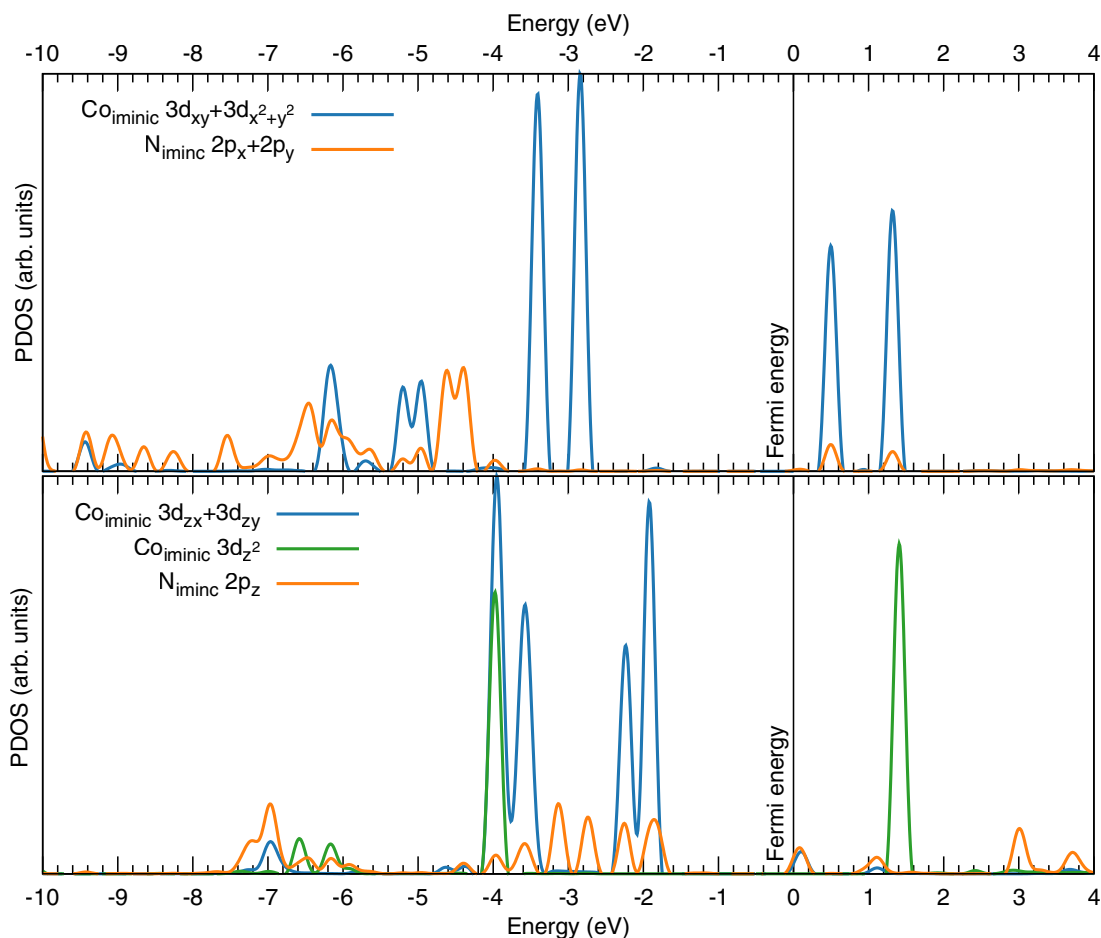


Figure 2.27: PDoS on the iminic Co atom and surrounding N atoms in the CoTPyP-Co MOF. In the top panel are reported the projections on in plane atomic orbitals while in the bottom panel are reported the projections on out of plane atomic orbitals.

Co-N BONDING

To gain a deeper understanding of the origin of the inequivalency between the two Co species, was investigated the nature of the Co-N bonding, specifically in the CoTPyP-Co MOF.

figs. 2.27 and 2.28 present the PDoS on the iminic and pyridinic Co atoms, respectively, along with their surrounding nitrogens. In the top panels of these figures, where only PDoS on in-plane orbitals are depicted, it is evident that many common peaks are shared between N orbitals ($2p_x$ and $2p_y$) and Co orbitals ($3d_{x^2-y^2}$ and $3d_{xy}$). This is indicative of a hybridization of those orbitals and hence the formation of covalent bonds stabilizing the metal.

2.3. COMPREHENSIVE INVESTIGATION OF ELECTRONIC STRUCTURE

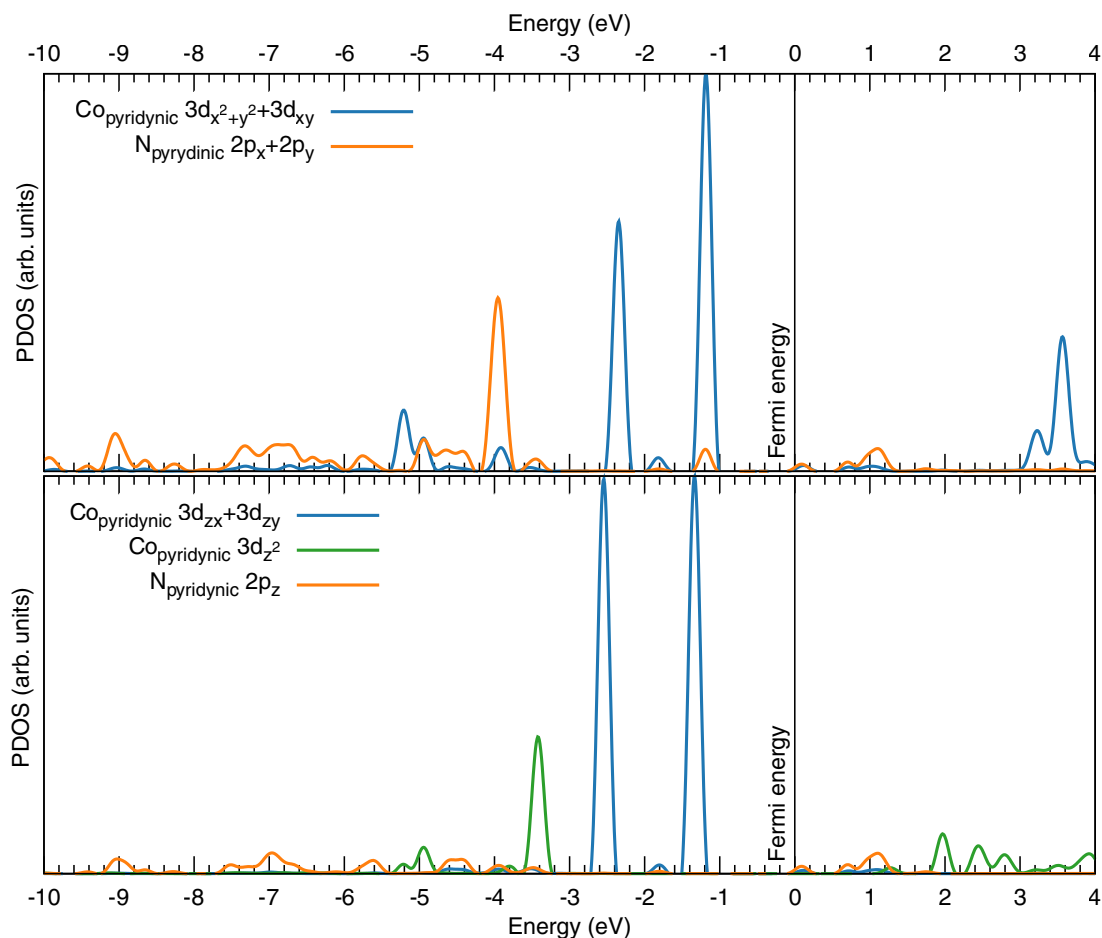


Figure 2.28: PDoS on the pyridyninic Co atom and sorrounding N atoms in the CoTPyP-Co MOF. In the top panel are reported the projections on in plane atomic orbitals while in the bottom panel are reported the projections on out of plane atomic orbitals.

Now, focusing on the PDoS of out-of-plane orbitals for the iminic center in the bottom panel of fig. 2.27, an overlap can be observed between nitrogen p_z and cobalt d_{zx} and d_{zy} peaks in the -4.2/-3.4 eV and -2.4/-1.8 eV ranges. This overlap suggests the presence of π bonding between these orbitals, further stabilizing the metal atom.

On the other hand, the Co d_{zx} and d_{zy} orbitals for the peripheral metal, which remain fully occupied, are not involved in bonding with the N atoms. This distinct behavior can be attributed to differences in Co-N distances. While the iminic center has a bond length of ~ 1.98 Å, the peripheral site exhibits an increased distance of ~ 2.12 Å. This greater distance prevents significant overlap between these orbitals. This observation is of paramount importance for the

reactivity of the two species. In one case, only the $3d_z^2$ orbitals are available for hybridization with an adsorbate molecule, while in the other case, the $3d_{zx}$ and $3d_{zy}$ orbitals are also available for bonding.

2.4 CHEMICAL REACTIVITY

2.4.1 CO ADSORPTION

The preceding section was dedicated to the differentiation of electronic properties between the two Co sites, hinting at potential variations in their reactivity. To investigate this hypothesis, the attention is now turned to the adsorption of Carbon Monoxide (CO) on these two sites.

Carbon monoxide is an inorganic molecule characterized by one of the strongest covalent bonds found in nature, boasting a dissociation energy of 11.11 eV [67]. Indeed, they are connected by a triple bond that consists in two π and σ bonds. Additionally, it possesses a small dipole moment of 0.122 D [68] but however can result in high adsorption energies upon chemisorption.

DFT RESULTS

Through our simulations of CO adsorption on the two catalytic sites, a significant disparity in adsorption energies has been unveiled. Specifically, the iminic site displayed a relatively modest adsorption energy of -0.45 eV, whereas the pyridinic site exhibited a stronger chemisorption (adsorption energy of -1.30 eV). Notably, this adsorption energy is comparable to the higher ones reported in the literature for CO adsorption on metallic surfaces [69].

To better understand the origin of this disparity, the attention is turned to the PDoS spectra for CO molecular orbitals and the vertical orbitals of cobalt (fig. 2.29). These spectra shed light on the electronic interactions at play.

In the case of CO chemisorption on the peripheral site, it becomes evident that the CO molecular orbitals overlap not only with the cobalt $3d_{z^2}$ but also with the $3d_{zx}$ and $3d_{zy}$ ones. This overlapping suggests that the σ molecular orbitals of CO form a covalent bond by hybridizing with the vertical d_{z^2} Co orbital. Simultaneously, the π orbitals of CO hybridize with d_{zx} and d_{zy} orbitals of cobalt. In contrast, this is not the case for the iminic site, where the CO orbitals solely overlap with the cobalt d_{z^2} orbitals. This difference in orbital interactions

2.4. CHEMICAL REACTIVITY

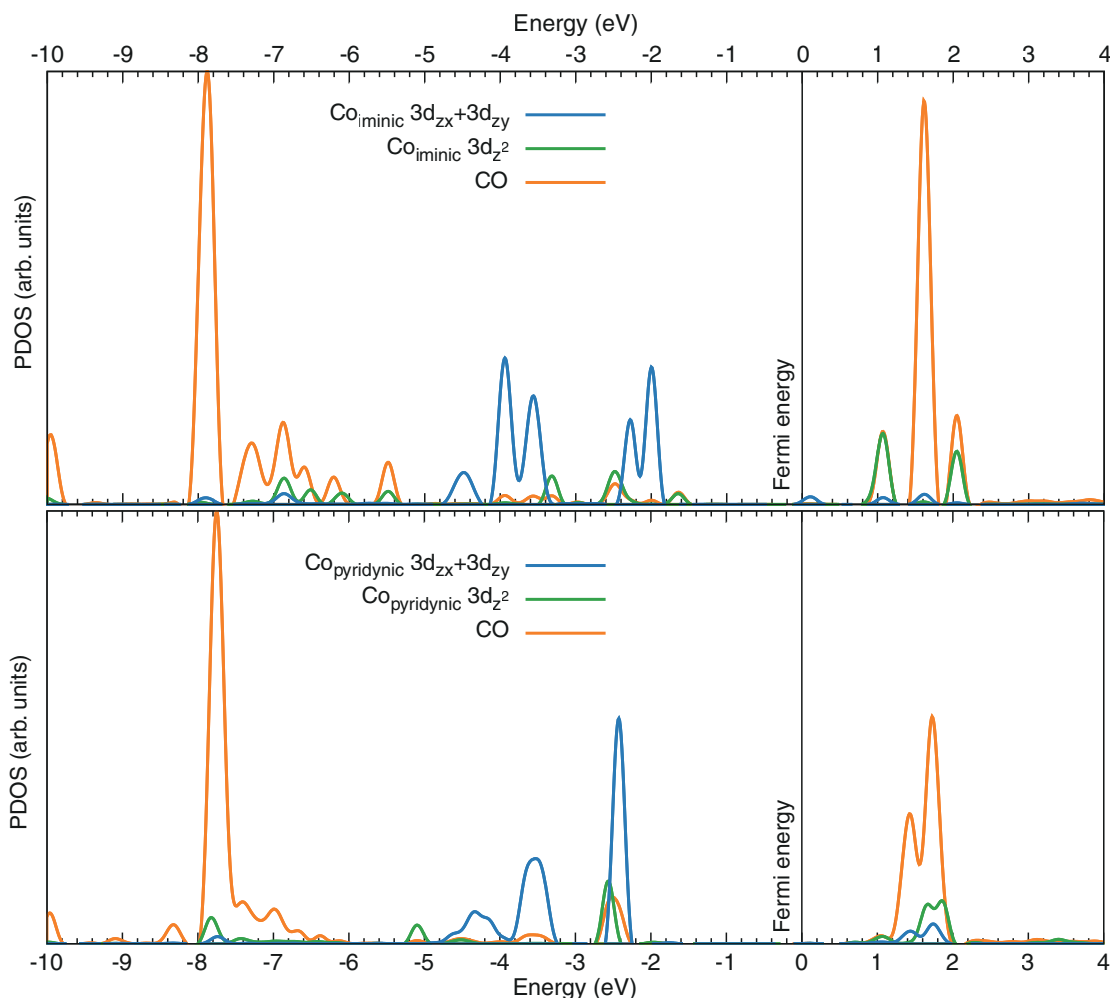


Figure 2.29: PDoS on the absorbed CO molecular orbitals and on Co $3d_{z^2}$, Co $3d_{zx}$ and Co $3d_{zy}$ orbitals for the adsorption of carbon monoxide on the iminic Co (top panel) and the peripheral Co (bottom panel)

is a key factor in the distinct stabilization of CO at these two sites.

However, a more profound reason for this variation lies in the fact that, as observed in the previous section, cobalt forms different bonds with the surrounding nitrogen atoms in the two sites. Within the macrocycle, where the Co-N distance is lower, d_{zx} and d_{zy} orbitals are involved in the bond with N atoms, thus precluding their availability for bonding with additional adsorbates. Conversely, these orbitals remain uninvolved in bonding with N atoms in the pyridinic site, allowing them to freely hybridize with the CO orbitals.

Furthermore, it is worth noting that, irrespective of the catalytic site, CO consistently adsorbs with its carbon atom bound to cobalt. However, there

is a crucial distinction in the orientation of CO adsorption. In the peripheral pyridinic configuration, CO adsorbs in a perfectly vertical alignment. This unique orientation results from the molecular π orbital hybridization of CO with the cobalt d_{zx} and d_{zy} orbitals. Conversely, within the macrocycle, where σ bonding between CO and the cobalt d_{z^2} orbital prevails, CO has the flexibility to tilt, deviating by approximately 35 degrees from the vertical axis.

EXPERIMENTAL EVIDENCES

Near-Ambient Pressure (NAP) Infrared-Visible Sum Frequency Generation (IR-Vis SFG) experiments were also carried on for both the monometallic and bimetallic systems. IR-Vis SFG, is a photon-in photon-out method that enables the study of vibrational modes of the system. It is particularly suitable for investigating heterogeneous catalysis due to its surface sensitivity and the long mean free path of photons in the gases.

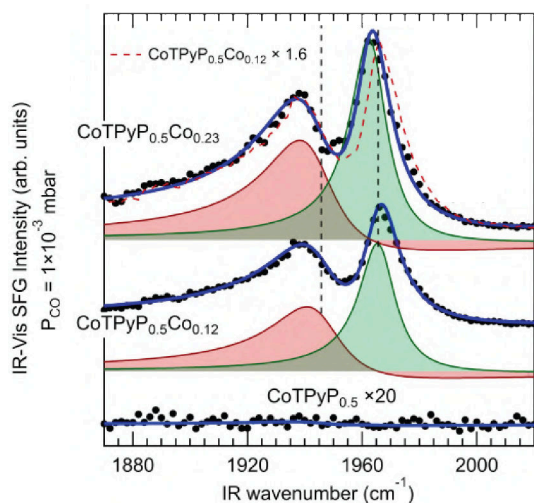


Figure 2.30: IR-Vis SFG spectra of $\text{CoTPyP}_{0.5}\text{Co}_x/\text{GR}/\text{Ir}(111)$ measured in situ with a CO pressure of 1×10^{-3} mbar, as a function of evaporated cobalt atom coverage.

The spectra, reported in fig. 2.30, plotted in the CO stretching range ($1800\text{--}2100\text{ cm}^{-1}$), were acquired as a function of the amount of peripheral cobalt atoms evaporated on a 0.5 ML $\text{CoTPyP}/\text{GR}/\text{Ir}(111)$ submonolayer and measured at constant CO pressure of 10^{-3} mbar at room temperature.

Starting from the bottom, the spectrum corresponding to the CoTPyP layer before cobalt exposure is completely flat, indicating that no CO adsorption occurs on the monometallic system. However, starting dosing Co, even at a 0.12 ML, corresponding to a $\text{CoTPyP}:\text{Co}$ ratio of about 8:1,⁴ two intense resonances arise. Those resonances further increase at higher

⁴Here, was taken into account the fact that not all the evaporated cobalt atoms are embedded in the MOF since some of them condense in large islands on GR.

2.4. CHEMICAL REACTIVITY

cobalt coverages. Already from this simple experiment, it could be concluded the very different chemical identities of the two cobalt species, and that the peripheral cobalt atoms are the only one active towards CO adsorption at that background pressure.

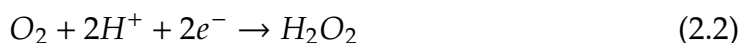
Moreover, experimental observations have confirmed the reversibility of this reaction with a complete CO desorption upon return to Ultra High Vacuum (UHV) conditions. This reversibility is a crucial and advantageous property for potential future applications of this system as a catalyst. It signifies that the catalytic system can endure numerous cycles of adsorption and desorption of reactants, which is a highly desirable characteristic for practical catalytic processes.

2.4.2 OOH-H₂O STABILIZATION

Both Oxygen Reduction Reaction (ORR) and Oxygen Evolution Reaction (OER) play fundamental roles in various technological applications, including fuel cells, metal-air batteries, and electrolyzers [70]. Focusing on ORR (which also applies to OER), it can proceed through two distinct pathways. Molecular O₂ can be reduced, leading to the formation of water via a 4-electron pathway:



Alternatively, O₂ can be reduced to form Hydrogen Peroxide (H₂O₂) via a 2-electron pathway:



In general, the formation of water via the 4-electron pathway is favored, considering the Nernst standard potential of the two reactions [70]:

$$E_{4e^-}^0 = 1.229V \quad E_{2e^-}^0 = 0.695V \quad (2.3)$$

While hydrogen peroxide (H₂O₂) has various important applications, such as bleaching, water treatment, and the production of organic compounds [71], it is often an unwanted side-product in some applications, such as metal-air batteries [72]. Therefore, a deeper understanding of these reactions is essential for directing them along a preferential path.

The initial steps of these reactions can proceed in different ways, all leading

to the formation of an adsorbed OH group [70]:

- Dissociative adsorption of O_2 : O_2 immediately breaks apart upon adsorption on the catalyst surface, forming two adsorbed oxygen atoms. These oxygen atoms interact with H^+ ions in solution, resulting in two adsorbed OH species. This process requires a high charge transfer into the oxygen molecule to cleave the bond [71].
- Associative adsorption of O_2 : O_2 adsorbs on the surface, often vertically, without breaking the bond. The molecule then interacts with H^+ ions in solution, forming an adsorbed hydroperoxyl OOH species. Only at this point does the O-O bond break, forming an adsorbed OH group and a second adsorbed oxygen atom. A second proton in solution can then bond to the adsorbed OH to form water.
- Peroxo mechanism: Similar to the associative mechanism, an OOH species is formed. However, in this case, an additional H^+ ion in solution can bond to the OOH group, forming a peroxo H_2O_2 molecule.

It has been demonstrated that the catalytic surface can influence the initial step of the reaction, favoring either the dissociative or associative mechanism. For example, C-coated Pt surfaces can enhance the formation of H_2O_2 , favoring an associative mechanism [73].

However, after the first reaction step, the reaction can proceed to form either water or hydrogen peroxide. Since its first observation [74], the hydroperoxyl (Hydroperoxyl radical (O_2H)) has gained the widely accepted role of a fundamental reaction intermediate, being involved at this point in the reaction of O_2 with water [75]. The O_2H radical can steer the process along a preferential path, resulting in significant differences in reaction kinetics and final products. It represents the key to a thorough understanding of the ORR mechanism and its control.

Many computational studies describe the stability of this species, its bonding geometry to catalytically active metal sites, and the energetics of the fundamental ORR reaction steps [76, 71, 77]. The influence of solvation is examined in detail at the fundamental level, but only in the gas phase, providing insights into the stability and properties of O_2H-H_2O clusters [78, 79, 80, 81, 82]. Evidence of the formation of O_2 and its role in the ORR was obtained on single-crystal Pt terminations, leaving an open question about the role of solvation in this reaction [83, 84].

Here are reported the evidences of the formation of O_2H-H_2O during ORR on the CoTPyP layer. The adsorption of a single O_2H and the whole O_2H-H_2O complex on a CoTPyP molecule was studied and the mechanisms behind the stabilization of the complex were elucidated.

2.4. CHEMICAL REACTIVITY

EXPERIMENTAL EVIDENCES

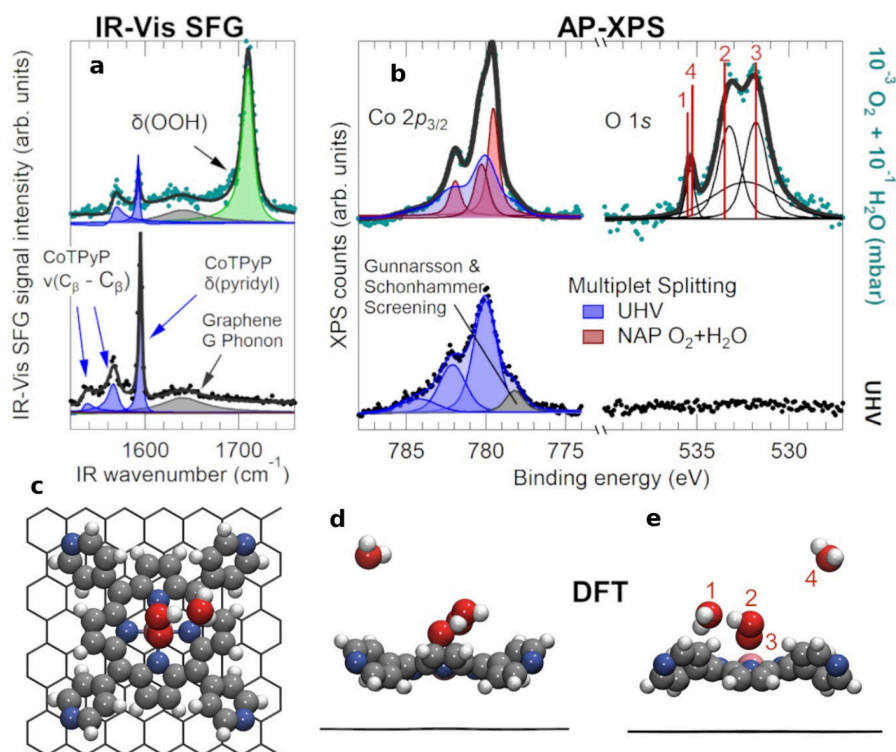


Figure 2.31: Spectroscopic and geometric characterization of the hydroperoxyl-water complex. (a) IR-Vis SFG spectra of the pristine CoTPyP/GR layer in UHV (bottom) and in 10^{-3} mbar O₂ + 10^{-1} mbar H₂O at room temperature (top); experimental data (markers) are reported together with the best fit (continuous lines) and deconvolution envelopes (filled profiles). (b) Near-Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS) spectra of the Co 2p_{3/2} (left, $h\nu = 910$ eV) and O 1s (right, $h\nu = 660$ eV) core levels; red vertical lines indicate the binding energies obtained for the optimized O₂H-H₂O complex on CoTPyP/GR from *ab initio* DFT calculations for different O 1s core levels, as labeled in (e): 1 - physisorbed/wetting water, 2 - OOH, 3 - OOH, 4 - gas phase water. (c) Top view of the DFT optimized model of the O₂H-H₂O/Co/TPyP/GR system. (d,e) Side views of the same system with an additional water molecule in the gas phase from two different points of view.

In order to investigate the system, two main experimental techniques were employed: NAP-XPS and IR-Vis SFG. From an experimental perspective, exposing the 2D system at room temperature to a NAP of 10^{-3} mbar of O₂ or 10^{-1} mbar of H₂O did not result in substantial vibrational (IR-Vis SFG) or electronic (NAP-XPS) spectroscopic modifications compared to the pristine layer. However, when the surface was exposed to a mixture of the two gases (fig. 2.31, panel

A), significant changes occurred. Although there was only a slight energy shift in the resonances associated with the CoTPyP/GR layer, a new, highly intense resonance at a higher frequency was observed. This resonance can be associated with a bending mode of the hydroperoxyl molecule [79, 80].

The exposure of the CoTPyP monolayer to the oxygen/water mixture also led to the growth of O 1s core level components in the NAP-XPS spectrum (fig. 2.31, panel B). Here, a contribution from gas phase molecules at 535.4 eV [85] could be clearly distinguished, along with two distinct features. These latter features were observed to grow in parallel and with almost equal intensity as a function of background gas pressure, suggesting that they are associated with the two oxygen atoms in the OOH species.

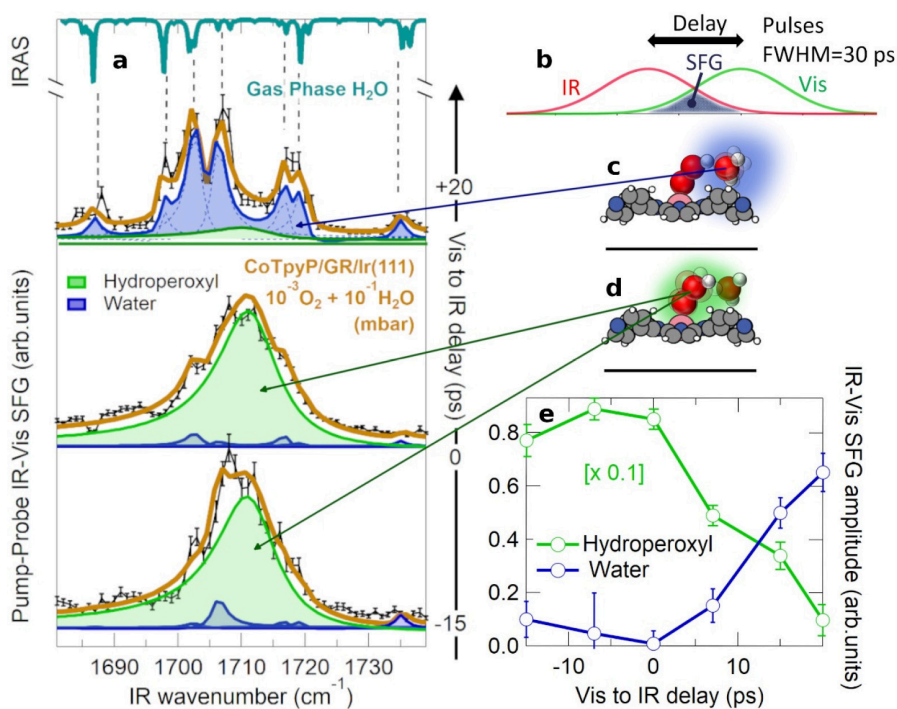


Figure 2.32: Energy coupling and stabilization of the ligated hydroperoxyl-water cluster. (A) IR-Vis SFG spectra of the evolution of the bending mode of OOH line shape at 1710 cm^{-1} as a function of the visible and Infrared (IR) pulses delay; In the top part, IR roto-vibrational spectrum of gas phase water [86]; (B) Sketch of the delayed IR and Vis pulses used to generate the time-resolved SF signal. (C,D) Best structural model of the $\text{O}_2\text{H-H}_2\text{O/CoTPyP/GR}$ system as obtained from DFT calculations (fig. 2.31, panels C-E), evidencing the contribution of the different moieties to the spectral evolution reported in (A); (E) Normalized IR-Vis SFG amplitude of the OOH and water modes obtained from the fit as a function of the IR-to-Vis delay.

2.4. CHEMICAL REACTIVITY

Furthermore, a pump-probe IR-Vis SFG experiment, where the SFG response is measured as a function of the delay between IR and visible pulses, was performed (fig. 2.32). Focusing on the frequency range associated with the OOH bending mode, it can be observed that, upon changing the delay, the vibronic energy of this mode is transferred to the water roto-vibrational modes. This indicates a strong coupling between the hydroperoxyl species and co-adsorbed water.

DFT RESULTS

To confirm the creation of the $\text{O}_2\text{H-H}_2\text{O}$ complex and gain a deeper understanding of the mechanisms behind its stabilization on the CoTPyP/GR layer, DFT simulations were performed. Since the hypothesis was that the complex is stabilized by the macrocycle of CoTPyP, particularly the central Co atom, and the fact that computed molecular properties do not significantly change considering a single molecule or the CoTPyP layer, the simulations were performed on a single molecule adsorbed on GR.

Various adsorption configurations of a single OOH molecule and the entire complex were examined, with the most stable configurations (obtained upon system relaxation) reported in figs. 2.31 and 2.33. In all instances, the hydroperoxyl specie bonds with the Co atom of the macrocycle. Referring to the atom indexing in fig. 2.31, panel E, the energetically favored configuration involved $\text{O}^{(3)}$ binding to the metal site (Co-OOH), consistent with calculations on analogous model systems [77]. However, another stable configuration was predicted where $\text{O}^{(2)}$ binds (Co-O(H)O). The energy difference between these two configurations was only 160 meV, suggesting that both (Co-OOH and Co-O(H)O) could potentially be populated, depending on the temperature and local surrounding environment. Focusing on the most stable configuration (Co-OOH), was predicted an adsorption energy of -5.40 eV for the hydroperoxyl specie alone. Upon bonding, a significant charge transfer occurred, primarily involving the inner macrocycle and the adsorbed OOH (see fig. 2.33). Upon considering the physisorption of an additional H_2O molecule, further stabilization took place, reflecting in an adsorption energy of the whole complex to -6.12 eV. Considering that the complex in the gas phase is stable and has a binding energy of 0.50 eV, an additional 220 meV is gained during H_2O physisorption. In this process, a new substantial charge transfer occurred, involving not only the complex itself

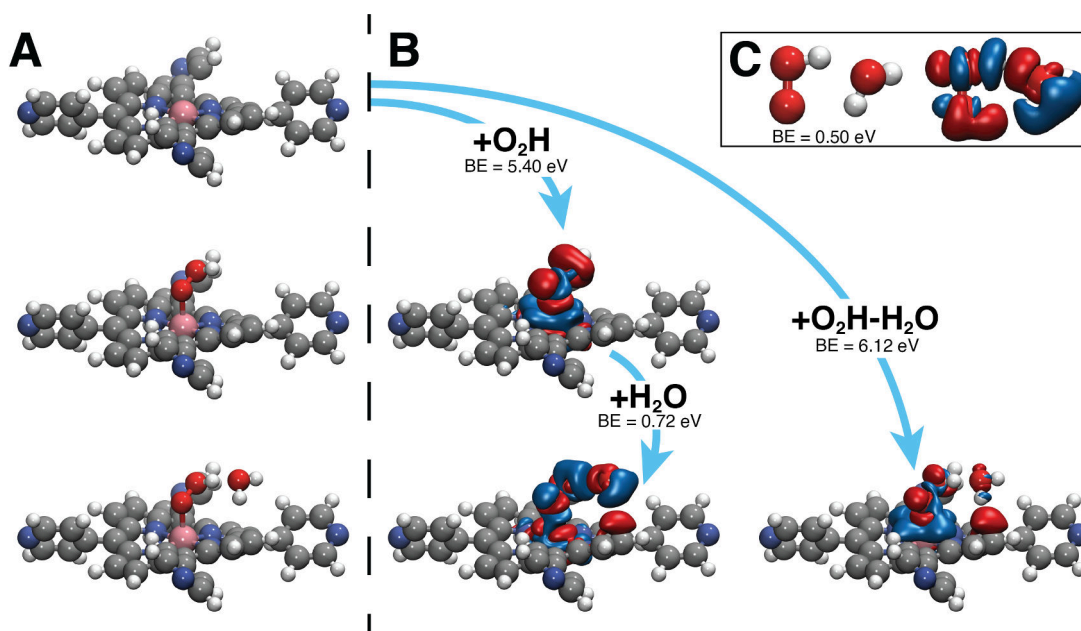


Figure 2.33: Insight on structural and electronic rearrangement for the $\text{O}_2\text{H-H}_2\text{O/Co}$ system. (A) From top to bottom, optimized models for CoTPyP/GR, $\text{O}_2\text{H/CoTPyP/GR}$, $\text{H}_2\text{O-O}_2\text{H/CoTPyP/GR}$, showing that CoTPyP is globally unaffected by the adsorption of O_2H and H_2O , apart from a small lifting of the Co atom by $0.16 \text{ \AA}$. (B) Bonding-induced rearrangement of the electron density distribution in the $\text{O}_2\text{H-H}_2\text{O/CoTPyP/GR}$ system, with respect to the individual constituents. Isosurfaces upon adsorption of: (left) first O_2H and then H_2O ; (right) the whole $\text{O}_2\text{H-H}_2\text{O}$ complex (red/blue for electron gain/loss, isovalues: $\pm 0.001 \text{ au}$). (C) Optimized configuration of the complex in gas phase, and electron charge redistribution upon complex formation-isosurfaces as in (B).

but also the Co-OOH bonding.

Examining the Löwdin charges, fig. 2.34 depicts the differences between the atomic charges of the whole system ($\text{O}_2\text{H-H}_2\text{O/CoTPyP/GR}$) and the two constituents separately ($\text{O}_2\text{H-H}_2\text{O}$ and CoTPyP/GR). It is evident that the inner macrocycle and the water molecule contribute by donating electrons to the OOH molecule, resulting in a gain of $0.15 e^-$. H_2O also induces a small charge accumulation on the nearest iminic and pyridinic rings, which evidently play a secondary role in the stabilization process.

2.4. CHEMICAL REACTIVITY

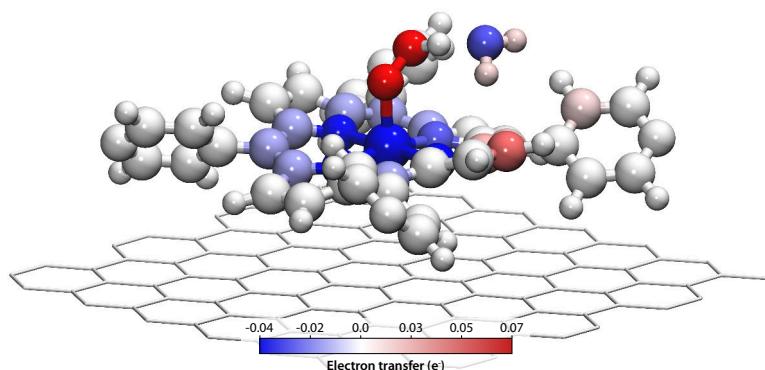


Figure 2.34: Charge redistribution in the $\text{O}_2\text{H-H}_2\text{O/CoTPyP/GR}$ system upon bonding of the $\text{O}_2\text{H-H}_2\text{O}$ complex to the CoTPyP/GR . The charge rearrangement is obtained from the difference of the Löwdin atomic charges between the entire system ($\text{O}_2\text{H-H}_2\text{O/CoTPyP/GR}$) and the two constituents separately ($\text{O}_2\text{H-H}_2\text{O}$ and CoTPyP/GR). The color of each atom indicates the amount of electron variation: red/blue correspond to electron gain/loss.

Despite the observed charge transfer towards the OOH species, there are no drastic electronic or geometrical changes detected in the radical. Simulations conducted for the isolated OOH reveal an O-O bond length of 1.35 Å and a magnetization of $+1.01 \mu_B$, indicating a doublet ground state typical of hydroperoxyl superoxide [87]. However, upon adsorption onto Co, only a minor increase in the O-O bond length to 1.39 Å is observed, accompanied by a partial reduction in the local magnetization to $0.59 \mu_B$. These findings suggest that upon adsorption on Co, the OOH still primarily functions as a superoxide rather than a metal-hydroperoxo complex, as the latter typically exhibits a singlet state and usually higher O-O bond lengths ranging from 1.40 to 1.55 Å [88, 89, 90, 91].

To compare with experimental XPS measurements, the CLS were computed for the O 1s core level for all the O atoms in the system, including a water molecule in the gas phase far away from the surface. The binding energy of O 1s for the gas phase H_2O molecule was set to the experimental value of 535.4 eV to establish an absolute reference for the other core level energies.

These results, presented in table 2.3, confirm that the two main peaks with similar heights in the experimental spectra (fig. 2.31, panel B) are related to the two O atoms of hydroperoxyl, while the other peak can be attributed to both the water in the gas phase and the "wetting" water. Furthermore, it can be observed that a better theoretical-experimental agreement can be obtained by

Atom	Exp	DFT	
		O ₂ H-H ₂ O	O ₂ H
1	535.4 eV	535.6 eV	
2	533.4 eV	533.6 eV	534.4 eV
3	531.8 eV	531.9 eV	532.1 eV
4	535.4 eV	535.4 eV	535.4 eV

Table 2.3: O 1s core level binding energies for the different O atoms in the O₂H-H₂O/CoTPyP/GR system. The atomic numbers refer to the labels in fig. 2.31, panel E. Experimental values are obtained from the deconvolution of spectra in fig. 2.31, panel B. DFT absolute values were obtained fixing the binding energy of the gas phase H₂O molecule to the experimental value of 535.4 eV and were computed considering the adsorption of the whole O₂H-H₂O and for just OOH radical.

considering the whole complex and not just the hydroperoxyl radical adsorbed on the CoTPyP layer.

To further investigate the bonding nature, fig. 2.35 displays the PDoS on the 2p orbitals of O, 3d_{z²} of Co, and 1s of H. Solid lines correspond to PDoS computed on the entire O₂H-H₂O/CoTPyP/GR system, while dashed lines represent the same PDoS curves for the pristine CoTPyP/GR configuration and the isolated O₂H-H₂O complex. Where selected two energy regions were no contribution from the isolated components (CoTPyP/GR and O₂H-H₂O) was present but a contribution from the bound system arises (depicted in orange and blue), and here was calculated the LDoS. Isosurfaces for these regions are depicted in fig. 2.36, panels A and B, where the hybridization between the Co 3d_{z²} and π orbitals of OOH is evident. Panel A also shows the charge delocalization between the O₂H-H₂O bond.

Furthermore, in fig. 2.36 panel C, the RDG isosurface is reported. Here, the high charge density between the O₂H-H₂O region indicates a strong hydrogen bonding between the two molecules. Additionally, moderate charge density is observed between the water molecule and the pyrrolic and pyridinic moieties of CoTPyP, indicating moderate noncovalent bonding that contributes to the stabilization of the complex.

In conclusion, by means of a combination of in situ measurements and theoretical methods, it was shown that a cobalt single-atom biomimetic model catalyst, based on a self-assembled monolayer of Co-porphyrins grown on an almost free-standing graphene sheet, stabilizes a hydroperoxyl-water cluster at

2.4. CHEMICAL REACTIVITY

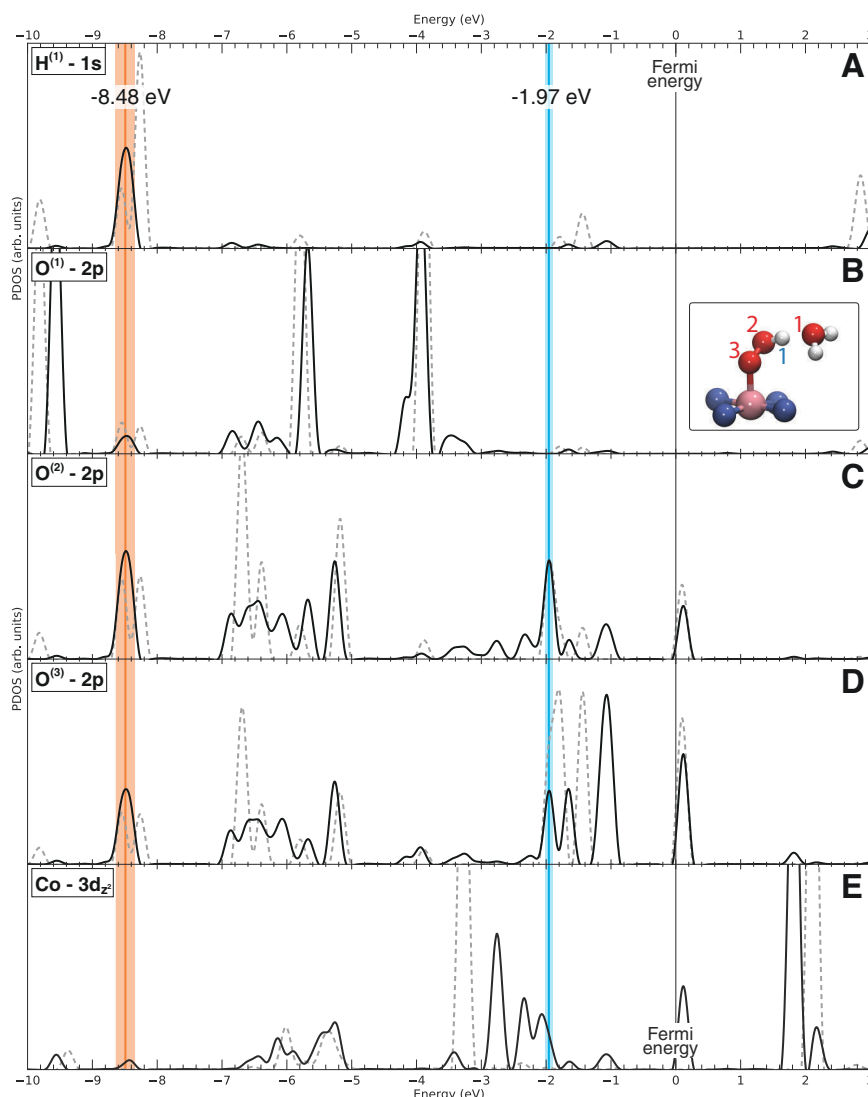


Figure 2.35: Calculated PDOS of the $\text{O}_2\text{H-H}_2\text{O/CoTPyP/GR}$ system. PDOS for some relevant atomic orbitals in the full $\text{O}_2\text{H-H}_2\text{O/CoTPyP/GR}$ system with the complex bonded to the porphyrin (solid black lines) and in the separated configurations of the constituents (pristine CoTPyP/GR layer and isolated $\text{O}_2\text{H-H}_2\text{O}$ complex, dashed grey lines) for: (A) 1s of H atom of hydroperoxyl molecule (multiplied by 3), (B-D) 2p of the three different O atoms of the complex (multiplied by 0.35) (E) $3d_{z^2}$ of Co atom of the porphyrin. Blue and orange vertical stripes identify selected energy ranges (orange: from -8.65 eV to -8.31 eV; blue: from -1.97 to -1.93 eV) characterized by the superposition of Co $3d_{z^2}$ and O 2p contributions in the bound configuration and not in the separated configuration, in order to highlight the orbital overlapping associated with chemical bonding. The LDoS integrated in the two energy windows and summed over all the relevant atoms is shown in fig. 2.36. The simulation for $\text{O}_2\text{H-H}_2\text{O}$ in gas phase was made leaving the molecular layer in the unit cell and moving away the complex, to guarantee the same reference energy for all the configurations.

room temperature in $\text{O}_2 + \text{H}_2\text{O}$ atmosphere. The interplay between charge transfer, dipole and H-bonding, and water solvation is found to determine ultimately the stability and bonding geometries, unveiling the core step of the ORR. This teases the mind toward a picture in which selectivity for 2e^- vs 4e^- ORR could be driven by the configuration of the hydroperoxyl ligand at the catalysts' active site, ultimately defined by the unraveled interplay between charge transfer, chemical, dipole, and H-bonding (solvation) phenomena, thus paving the way toward novel approaches to the reaction control.

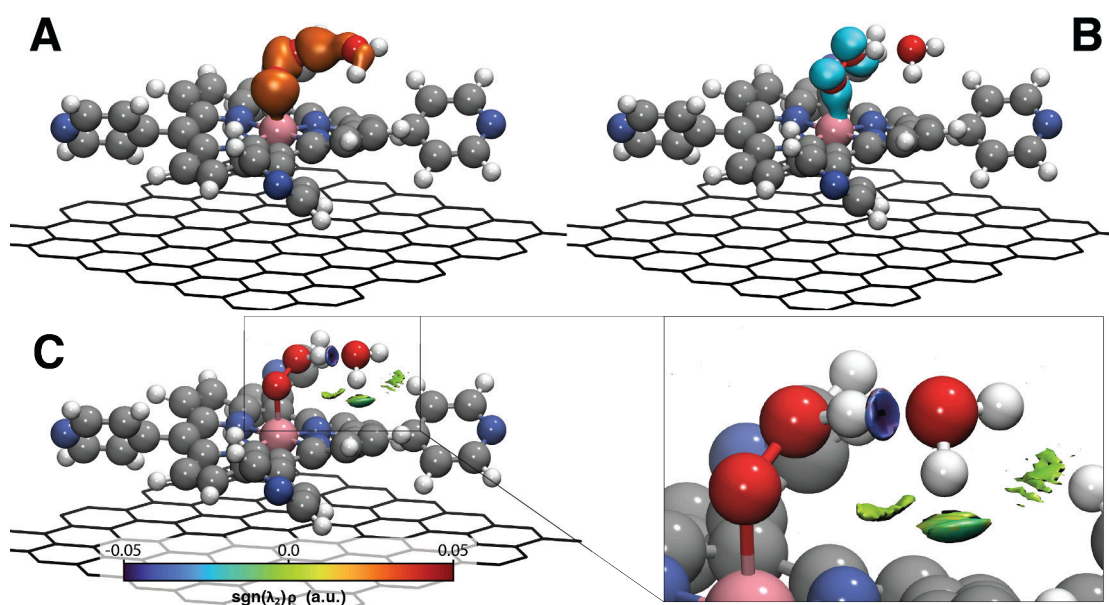


Figure 2.36: Insight on bonding nature stabilizing $\text{O}_2\text{H}-\text{H}_2\text{O}$ complex. (A, B) Spatially resolved LDoS integrated in two relevant energy ranges (fig. 2.35) (surfaces isovalue: 0.005 au). In (A) the charge accumulation in the $\text{O}_2\text{H}-\text{H}_2\text{O}$ bonding region is visible, and in both (A) and (B) the hybridization of the Co $3d_{z^2}$ and 2p orbitals of the terminal O atom of O_2H ($\text{O}^{(3)}$ in fig. 2.31). (C) Visualization of noncovalent interactions by means of an isosurface of the RDG: the blue color of the isosurface between O_2H and H_2O indicates a region with rather strong noncovalent bonding, and the green color of the isosurface between H_2O and the pyrrolic and pyridinic moieties of the CoTPyP indicates a region with moderate noncovalent bonding (RDG value: 0.6 a.u., with color depending on the local value of the electron density).

3

Transition Metal Dichalcogenides

3.1 BACKGROUND

Among the wide family of two dimensional and layered materials, TMDCs are an emerging class with properties that make them highly attractive for broad application prospects such as in nanoelectronics, optoelectronics, superconductivity. Generally, the layered TMDCs have chemical formula that can be expressed as MX_2 (ie, unit), comprising of a transition-metal element (M) and a chalcogen element (X).

Despite the same chemical formula, TMDCs exist in several structural phases resulting from different coordination spheres of the transition metal atoms. The two most common structural phases are characterized by either trigonal prismatic (2H) or octahedral (1T) coordination of metal atoms. Generally, they are constituted by van der Waals interacting layers formed by transition metal atoms sandwiched by covalently bonded chalcogens. These different phases can also be viewed in terms of different stacking orders of the three atomic planes (chalcogen-metal-chalcogen) forming the individual layers of these materials (fig. 3.1). The 2H phase is characterized by an ABA stacking order in which chalcogen atoms in different atomic planes occupy the same position A and are located on top of each other in the direction perpendicular to the layer. By contrast, the 1T phases are characterized by an ABC stacking order. Depending on the particular combination of transition metal and chalcogen elements, the thermodynamically stable phase at high temperature is usually either 2H or 1T.

3.2. PHASE TRANSITION IN VTe_2

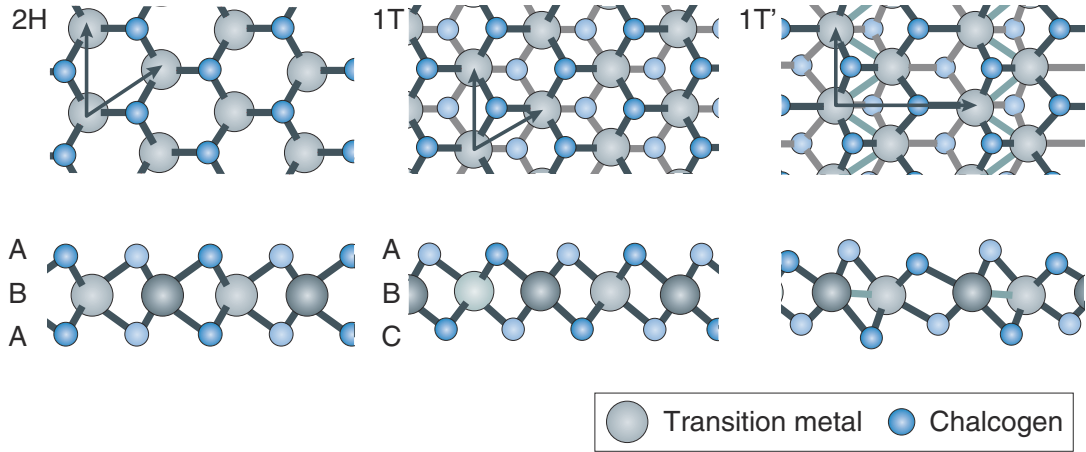


Figure 3.1: Single layer atomic structure of TMDCs in the trigonal prismatic (2H), distorted octahedral (1T) and dimerized (1T') phases. Image adapted from [92].

However, the structure of TMDCs is sensitive both to temperature and the number of layers. Indeed, at lower temperature they can undergo a phase transition to a distorted phase with higher periodicity (as the 1T' phase in fig. 3.1). The presence of this Periodic Lattice Distortion (PLD) is inevitably coupled with a spacial modulation of the electronic charge density, the so-called CDW. Indeed, it was demonstrated that a modulation of the charge density without a coupling to phonons cannot exist, therefore establishing the equivalence between CDW and the concept of periodic lattice distortions [92, 93].

The origin of this profound modification reflects on the electronic structure and must be sought in the large lattice reconstruction that breaks the rotational symmetry of the normal phases. Thus the control of the atomic motion of the atoms involved in the lattice reconstruction is expected to have a profound effect on the electronic modifications induced by the emergence of the CDW phase. For this reason CDW is widely studied since it could pave the way towards triggering exotic phase transitions and generating new functionalities. Indeed, in TMDCs such in TaS_2 , its manipulation could be realized by applying various external stimuli, such as pressure[94], electric fields[95] or optical pulses[96].

3.2 PHASE TRANSITION IN VTe_2

Among all the TMDCs, here the attention is focused on VTe_2 . His structural phase was observed to be highly sensitive both to temperature and the number

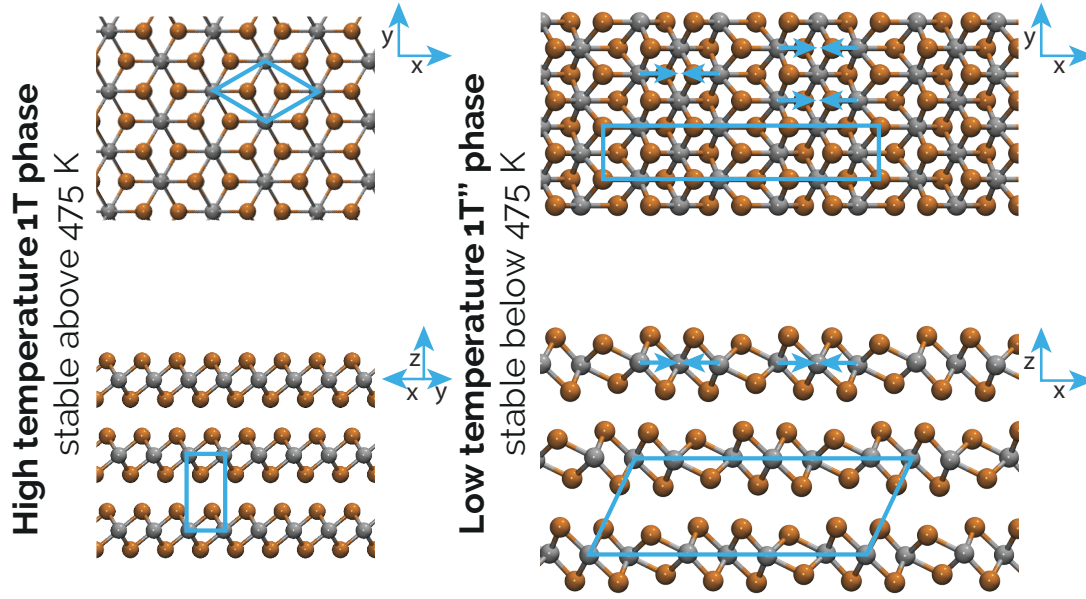


Figure 3.2: Stick-and-ball models for the stable structures of bulk layered VTe_2 . Unit cell for 1T phase and conventional cell for 1T'' structure are shown. The azure arrows indicate the direction of V atoms displacement in the 1T'' phase.

of layers. Indeed, a VTe_2 monolayer was reported to have a 1T phase at room temperature, while at cryogenic temperatures it undergoes a PLD to a 4×4 superstructure; conversely, a few layer (2-3) sample exhibits a 1T' phase [97]. However, our interest here is on the bulk material, which is characterized by a high-temperature 1T structure [98], that, upon cooling, undergoes a phase transition to a PLD phase (1T'') at around 475 K [98, 99].

Great scientific interest resides in the study of this phase, and the coupling with phonon modes that can pave the way towards its manipulation. Here, a first characterization of both 1T and 1T'' phases will be done. Furthermore, the attention is devoted to the coupling between phonon modes and CDW that was studied by means of both *ab initio* DFT calculations and Time-Resolved Optical Spectroscopy (TR-OS) experiments.

CHARACTERIZATION OF 1T AND 1T'' PHASES OF VTe_2

The high temperature 1T phase is constituted of trigonal layers formed by edge-sharing VTe_6 octahedra (fig. 3.2, left panel). This structure can be described in a trigonal cell (space group 164) containing 3 atoms and $a = b = 3.597 \text{ \AA}$ and $c = 6.699 \text{ \AA}$ lattice parameters. Those constants were obtained by means of DFT

3.2. PHASE TRANSITION IN VTe_2

variable-cell relaxation calculation using NCPPs and fixing the space group.

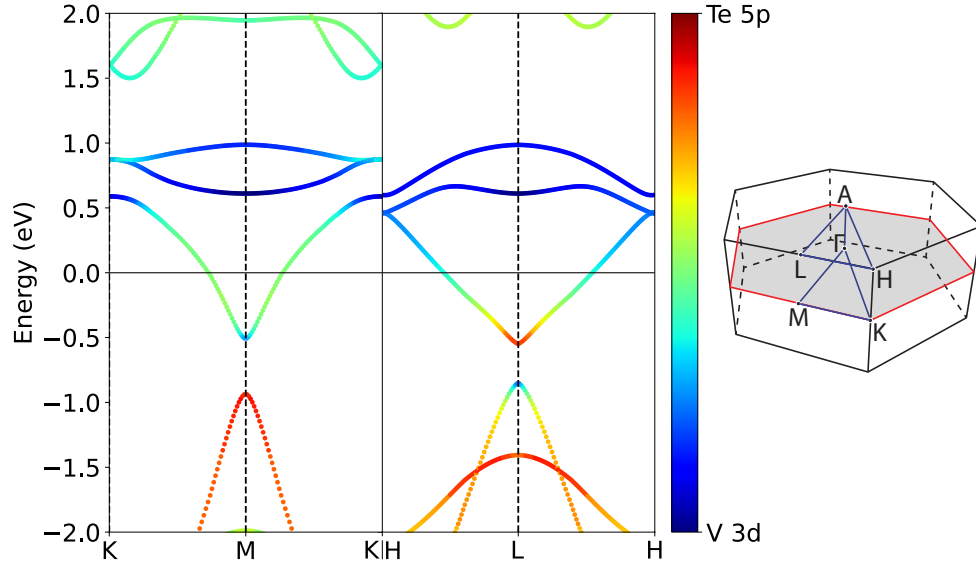


Figure 3.3: Band structure of bulk VTe_2 in the 1T phase along K-M-K path and on the same path at $k_z = \pi/c$. The color of the curves indicates the weight of orbital characters, as shown by the color scale. The Fermi level is set to zero. The Brillouin zone of the 1T phase is reported on the right.

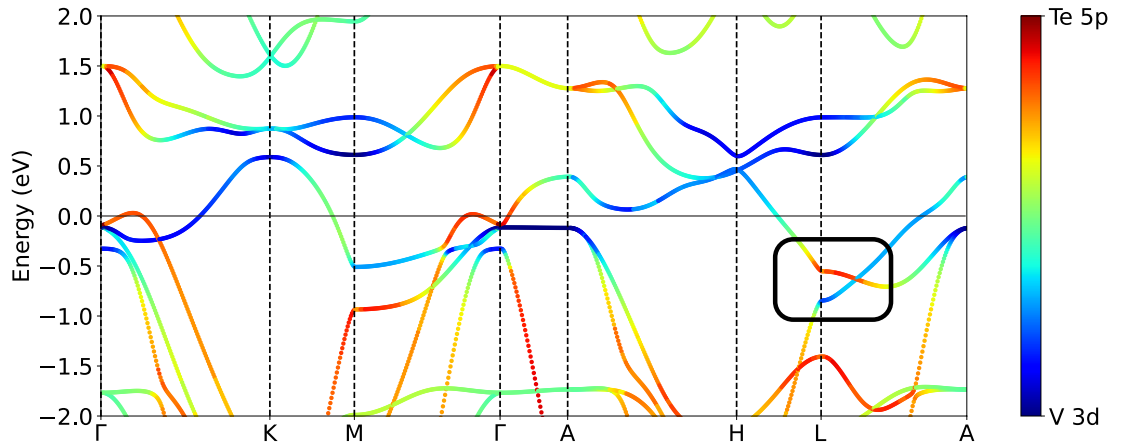


Figure 3.4: Band structure of bulk VTe_2 in the 1T phase along a high symmetry path. The color of the curves indicates the weight of orbital characters, as shown by the color scale. The black rectangle identifies a region of bands inversion; here the gap between the two states is closed due to the absence of Spin-Orbit Coupling (SOC). The Fermi level is set to zero.

The band structure of this phase is characterized by Dirac-like states located at around 0.6 eV below Fermi energy along K-M-K and centered at M points. The

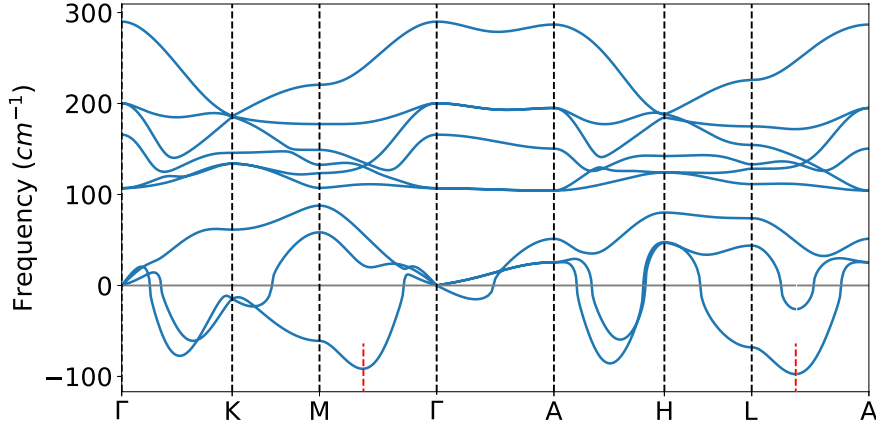


Figure 3.5: Phonon dispersion for VTe_2 in the 1T phase along a high symmetry path. The negative frequency modes reflect the instability of the system in this phase at low temperature. The red dotted lines highlight the $\mathbf{q}$ points where the deepest instability occurs. These points are located at around $2/3$ of Γ -M and A-L paths suggesting that the system would form a superstructure with a $(3 \times 1 \times 1)$ periodicity.

band structure along this path is reported in the left panel of fig. 3.3. Here, a false color scale is used to show the weight of the atomic orbitals as obtained from the projection of Kohn-Sham states on the atomic orbitals performed by `projwfc.x` executable. Furthermore, comparing the band structure along K-M-K path with the one along the same in-plane path but at $k_z = \pi/c$ (right panel in fig. 3.3), it is possible to observe that a band inversion occurs involving vanadium 3d and tellurium 5p contributions between M and L points. This observation suggests a metallic topological character of the system.

Considering the band structure in fig. 3.4, computed along a different high symmetry path, the same band inversion can be identified in proximity of M and L points. In the black rectangle, along L-A path, it can also be observed the closing of the gap between these states. This is due to the fact that all the calculations presented in this work were performed without taking into account for SOC. Indeed, as reported by Mitsuishi and coworkers [100], the SOC is a fundamental ingredient leading to the opening of a gap of about 0.1 eV between the two bands involved in the inversion. Moreover, by means of slab calculations they could demonstrate the growth of a metallic surface state in this region, which is topologically protected by this band inversion.

However, this phase is stable only at high temperature, while in DFT calculations, it is considered at 0K, forcing the system to be in the 1T phase. This clearly

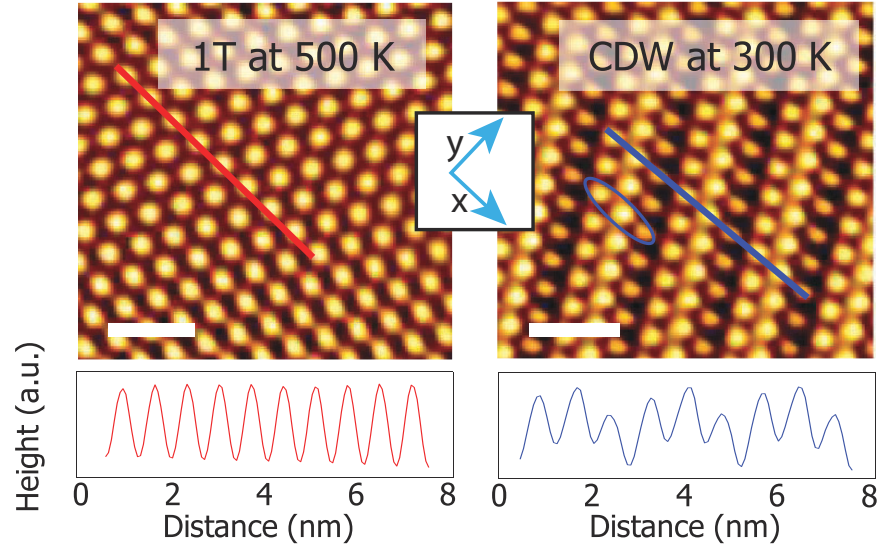


Figure 3.6: STM images of a VTe_2 single crystal at $T = 300$ K (left) and at $T = 500$ K (right) with a tunneling current of 1 nA and a voltage of 0.4 V. Blue ellipse highlights the vanadium trimerization. Adapted from [103]

reflects in the phonon dispersion reported in fig. 3.5 in the imaginary phonon modes. Those modes are a clear signature of the instability of the system in this phase at low temperature.

Interestingly, it can be argued that the CDW spatial modulation can be inferred from the $\mathbf{q}$ point where the deepest instability occurs in the phonon calculations [101, 102]. In this case, it is located at around $2/3$ of Γ -M and A-L paths (highlighted by the red dotted lines in fig. 3.5), suggesting that the low temperature $1T''$ phase is characterized by a $(3 \times 1 \times 1)$ superstructure with respect to the normal phase, which is in agreement with the experimental evidences [98].

Indeed, the low temperature $1T''$ phase (reported in the right panel in fig. 3.2 together with its conventional unit cell) forms a monoclinic (space group 12) structure containing 9 atoms and has optimized cell parameters $a = 18.984 \text{ \AA}$, $b = 3.595 \text{ \AA}$, $c = 9.069 \text{ \AA}$ and $\beta = 133.3^\circ$. During the phase transition the threefold rotational symmetry of the normal phase is broken, and the vanadium atoms are displaced along the x axis. This displacement is reported in fig. 3.2 by the azure arrows and is accompanied by a contraction of the metal-metal bond length of 9.5% from $3.60 \text{ \AA}$ to $3.26 \text{ \AA}$, in agreement with the experimental evidences [98]. This contraction is particularly evident also from the experimental STM images available in literature [103] for the two phases (fig. 3.6). Here, a trimerization of

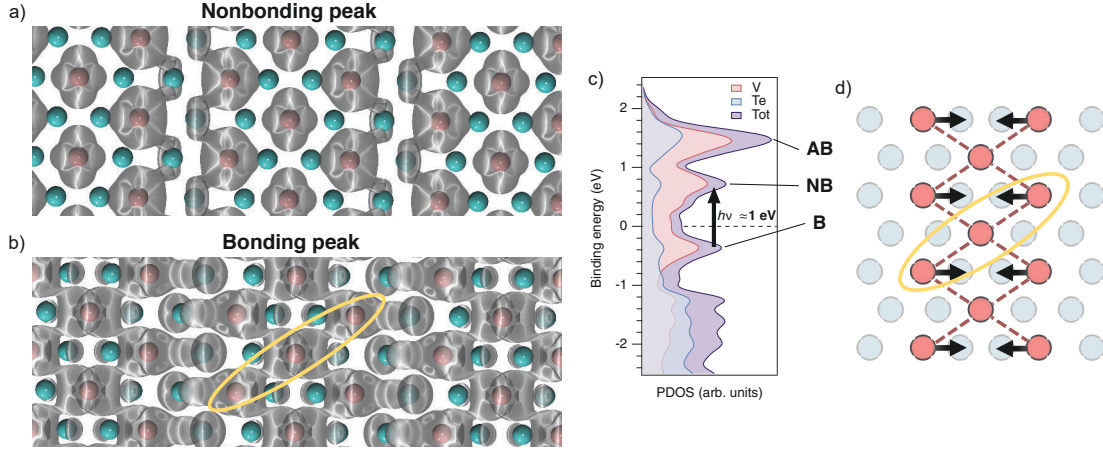


Figure 3.7: ILDoS isosurfaces for the $1T''$ phase. (a) ILDoS computed in a 0.1 eV energy range centered at the non bonding (NB) peak at 0.7 eV in the DoS in panel (c). (b) ILDoS computed in a 0.1 eV energy range centered on the bonding (B) peak at 0.3 eV below Fermi energy. (c) DoS around Fermi energy highlighting the peaks associated to bonding, non bonding and antibonding (AB) orbitals. (d) Schematic model showing a top view of a $1T''$ phase VTe_2 layer. The yellow oval, reported also in panel (b), highlights the formation of trimerized vanadium atoms.

vanadium atoms is clearly visible in the $1T''$ phase, which leads to the formation of parallel rows with double zig-zag chains along the y axis.

The trimerization mentioned above is particularly evident looking at the ILDoS isosurfaces (fig. 3.7, panels (a) and (b)) acquired in an energy range of 0.10 eV centered around -0.30 eV (panel (a)) and +0.70 eV (panel (b)). Referring to the PDOS reported in panel (c), it corresponds to the bonding (B) and nonbonding (NB) peaks. In particular, the B ILDoS highlights the charge delocalization between trimerized V atoms (in the yellow oval), while the NB ILDoS shows a higher localization on vanadiums reflecting the behaviour observed in the experimental STM image (fig. 3.6).

Due to this PLD, giving rise to a CDW and to the breaking of the original symmetry of the system, the three equivalent M points in the Brillouin zone of the $1T$ phase turn into two inequivalent M_1 and M_2 points in the $1T''$ phase. While the Dirac-like states remain present at M_1 , at M_2 they vanish giving rise to flatter bands (fig. 3.8). Hence, the transition between these two phases induces a directional change of the electronic structure of the system, which also breaks the topological character of the $1T$ phase.

3.2. PHASE TRANSITION IN VTe₂

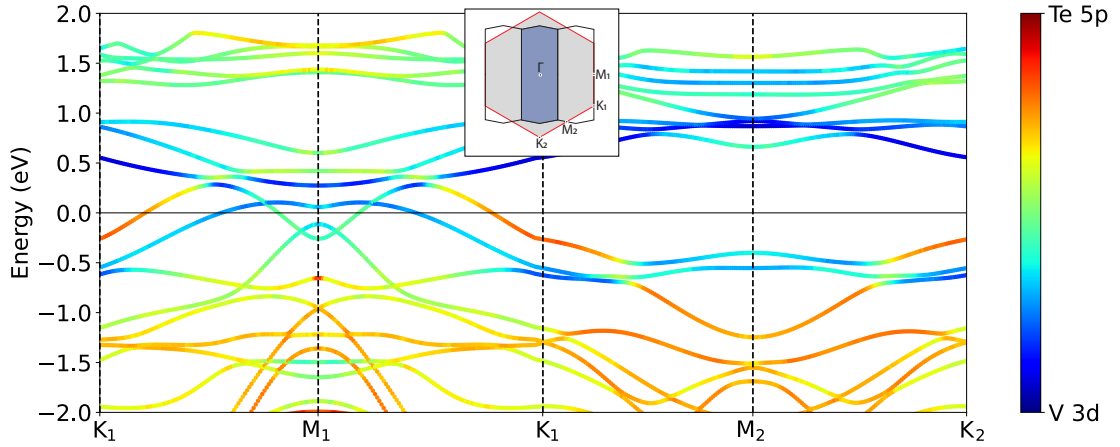


Figure 3.8: Band structure of bulk VTe₂ in the 1T phase along the K-M₁-K-M₂-K path evidencing the directional change induced by the phase transition. The color of the curves indicates the weight of orbital characters, as shown by the color scale. The Fermi level is set to zero. The inset reports a slice of the Brillouin zone passing through the Γ and perpendicular to $\mathbf{k}_z$ of the 1T'' phase (light blue) and of the 1T phase (gray).

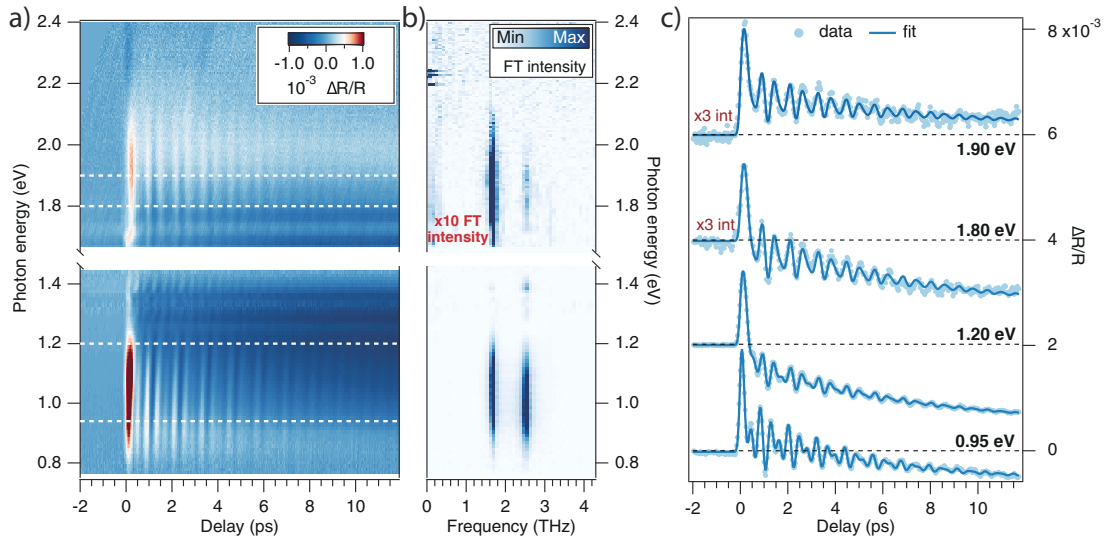


Figure 3.9: (a) Two dimensional map showing the evolution of the relative reflectivity $\Delta R/R$ signal of VTe₂ as a function of pump-probe delay and of the probe photon energy. (b) Two dimensional map showing the magnitude of the Fourier transform of the $\Delta R/R$ signal extracted from (a) as a function of the frequency and the probe photon energy. (c) Traces extracted from (a) showing the evolution of the $\Delta R/R$ signal as a function of the pump-probe delay for four selected probe photon energies.

PHONON MODES AND CDW COUPLING

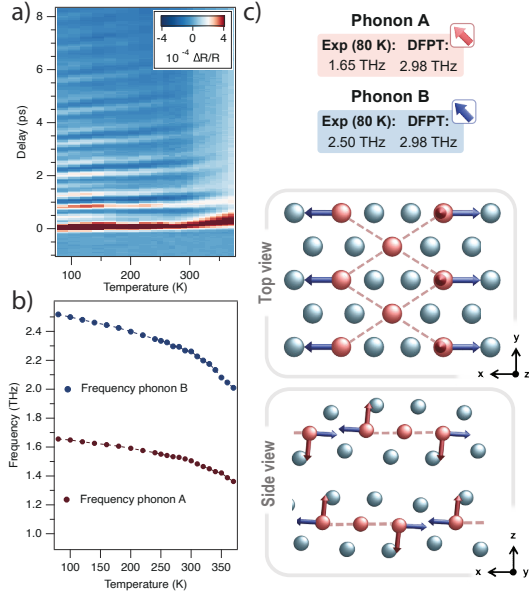


Figure 3.10: (a) Two dimensional map showing the evolution of the $\Delta R/R$ signal as a function of the temperature and of the pump-probe delay. The measurements have been performed at a probe photon energy of ~ 0.95 eV (1300 nm). (b) Evolution of the frequency of the two phonon modes as a function of the temperature. (c) Schematic representation of the displacements of the vanadium atoms associated with phonon A (red arrows) and phonon B (blue arrow). Vanadium atoms are in red, tellurium atoms are in teal. The colored boxes show a comparison between the experimental and the calculated frequency of the two phonon modes.

are strongly affected by the emergence of the CDW phase. The fact that a strong enhancement in the amplitude of the oscillation occurs at these energies is a first evidence of the link among those phonon modes and their interplay with the CDW phase.

From an experimental point of view, a single crystal VTe_2 sample was investigated by means of TR-OS, measuring the relative reflectivity changes ($\Delta R/R$) caused by the collective and single particle excitations in the low-temperature CDW phase. The evolution of reflectivity as a function of the pump-probe delay measured at 80 K is reported in fig. 3.9 panel (a) together with its Fourier Transform in panel (b). Here two sharp peaks at a frequency of ~ 1.65 THz and ~ 2.50 THz appear over a wide range of phonon energies. In order to distinguish between the two, the low frequency will be labelled as mode "A", while the other as mode "B".

From single traces extracted from fig. 3.9 panel (a) and reported in panel (c), for energies below 1.3 eV, a strong beat between the two modes is clearly visible, while for higher energies there is a predominant contribution of phonon A. Indeed, for energies of ~ 1 eV the probe beam is resonant with the transition between hybridized bonding and non bonding vanadium states above the Fermi level (fig. 3.7, panel (c)) which are

3.3. TOWARDS A MACHINE LEARNING BASED STUDY OF PHASE TRANSITION

In order to deeply understand the interplay between the PLD and the phonon modes, fig. 3.10, panels (a) and (b) report the pump-probe reflectivity map and the extracted phonon frequencies as a function of temperature. A strong renormalization of the frequency of the two modes occurs upon increasing the temperature towards the CDW critical temperature.

The computed eigendisplacements of the two phonon modes for the vanadium atoms involved in the CDW reconstruction are reported in fig. 3.10 panel (c). For both modes there is a component of the motion along the direction of the PLD (x-axis in this figure), meaning that both can manipulate the amplitude of the CDW. However, even if, both phonons are intertwined with the CDW, for phonon B the movement of the vanadium atoms is more localized along the direction of the PLD and therefore it is expected to have a stronger coupling with the CDW. This observation is in agreement with the fact that this mode shows a more pronounced temperature renormalization of the frequency, meaning that it is more sensitive to the CDW disappearance. Conversely, phonon A involves smaller displacements along the lattice reconstruction and more pronounced out of plane movements.

3.3 TOWARDS A MACHINE LEARNING BASED STUDY OF PHASE TRANSITION

3.3.1 FORCE CONSTANTS FOR VTe_2

Up to this point, the two phases of VTe_2 have been considered separately, and for both phases, only the ground state properties at 0 K have been calculated. However, a future perspective involves studying the system as a function of temperature, spanning the phase transition through molecular dynamics simulations.

This would be a challenging task to achieve just using AIMD. Therefore, a potential alternative approach could involve the use of machine learning techniques to develop an IP for the system based on short AIMD trajectories. Subsequently, this IP could be employed to conduct classical molecular dynamics simulations.

When approaching the problem in this manner, a fundamental question arises: how large should the simulation cell be to ensure the accurate repro-

duction of the phase transition? Additionally, in the training procedure, how should one choose the value of the cutoff radius r_C within which to consider the interatomic interactions?

In this context, an attempt was made to establish criteria for addressing these questions in advance, without the need to develop an IP and then perform testing. Indeed, while the training process is relatively inexpensive, especially when the codes are parallelized across multiple GPUs, AIMD simulations are computationally demanding. Therefore, a crucial consideration is to select a supercell size as small as possible in order to reduce the computational effort. To address this, a preliminary study was conducted on the 1T phase of VTe₂ by investigating how the force constants decay with distance.

By calculating the phonon dispersion reported in fig. 3.5, DFPT provides the real-space force constants matrix $D_{\alpha\beta}^{(lmn)}(i, j)$. This matrix represents the second derivative of the total energy concerning the atomic displacements along the α direction of atom i in the unit cell and along the β direction of atom j in the replica of the unit cell (lmn) along the lattice vectors **a**, **b**, and **c**.

$$D_{\alpha\beta}^{(lmn)}(i, j) = \left. \frac{\partial^2 E}{\partial u_{\alpha}^{(lmn)}(i) \partial u_{\beta}^{(000)}(j)} \right|_{\mathbf{u}=0} \quad (3.1)$$

In the case under study, since the phonon calculation was carried on employing a $6 \times 6 \times 4$ **q** grid, $l < 6$, $m < 6$ and $n < 4$, while $i, j < 3$ being the atomic index in the unit cell. In order to simplify the analysis, a new matrix $\tilde{D}$ was defined by condensing the information about the displacement directions as:

$$\tilde{D}^{(lmn)}(i, j) = \frac{1}{3} \sum_{\alpha} \sqrt{\sum_{\beta} \left[D_{\alpha\beta}^{(lmn)}(i, j) \right]^2} \quad (3.2)$$

Furthermore, since the interest resides in how these force constants decay with the distance between the atoms, $\tilde{D}$ was expressed as a function of the distance $|\mathbf{r}|$ between the atom i in the unit cell and the atom j in the replica of the unit cell (lmn) , $\tilde{D}^n(|\mathbf{r}|)$. This was done by taking into account for the PBC by means of minimum image convention. To account for the 2D layered nature of the system, the dependence on the index n was maintained, providing information about whether the two atoms are on the same layer, one layer apart, or two layers

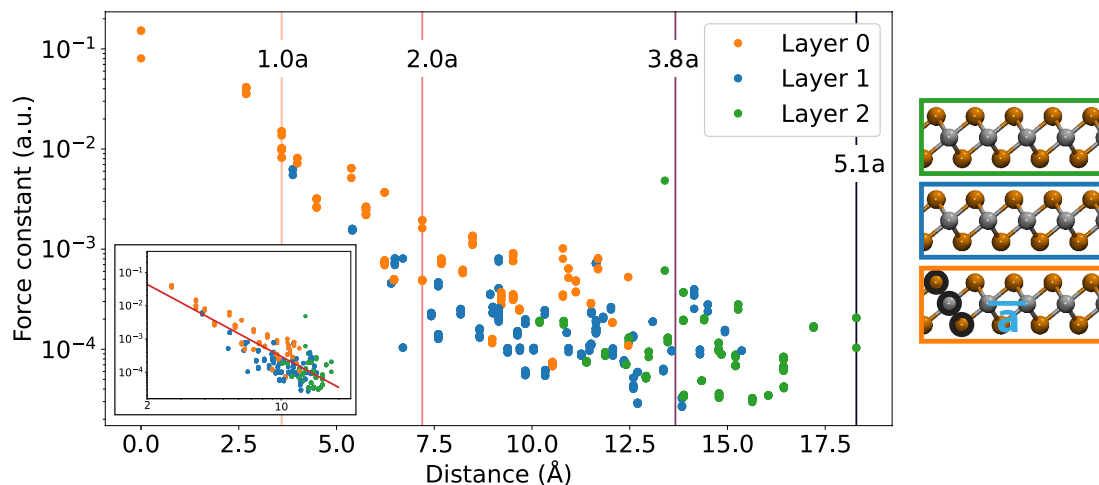


Figure 3.11: Behavior of interatomic force constants as a function of distance between atomic pairs, which were computed using DFPT on a $(6 \times 6 \times 4)$ $\mathbf{q}$ grid for bulk VTe_2 in 1T phase. Different colors represent force constants arising from atoms located on the same layer, one layer apart, or two layers apart, as shown in the stick-and-ball model on the right. One atom of the pair is consistently positioned in the unit cell and is indicated by a black contour in the atomic model. Vertical lines mark the cutoff radii r_C used to generate the phonon dispersions in fig. 3.13. In the inset is reported a *log-log* plot of the force constants with the fit function $f(r) \propto |r|^{-3.10}$ (red line).

apart¹. In fig. 3.11, the force constants are depicted as a function of distance. A clear power-law decay, approximately proportional to $|\mathbf{r}|^{-3}$, can be recognized (inset in fig. 3.11). This decay pattern remains consistent for interactions both within and outside the plane, albeit with a slight reduction of force constant within the same distance for more distant layers. This behavior aligns with a $\propto |\mathbf{r}|^{-2}$ decay characteristic of van der Waals interactions between infinite planes. However, a notable exception occurs at a long distance of $13.9 \text{ \AA}$, associated with the displacement of a V atom in the unit cell and a V atom with the same in-plane coordinates located two layers above.

To verify if this effect might be an artifact resulting from the finite size of the supercell², a secondary calculation was conducted using a $6 \times 6 \times 8$ $\mathbf{q}$ point grid, corresponding to a $6 \times 6 \times 8$ supercell in real space. The results,

¹It should be noted that due to PBC also in the vertical direction, even if the supercell is four layers high, atoms are at most two layers apart from each other.

²Notably, the vanadium atom in the second layer is equidistant between a V atom in the unit cell and its periodically repeated image along the z axis.

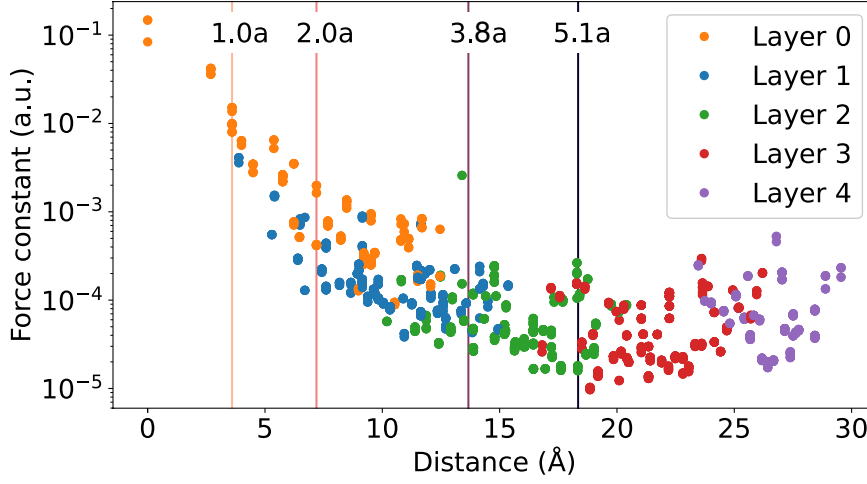


Figure 3.12: Behavior of interatomic force constants as a function of distance between atomic pairs, which were computed using DFPT on a $(6 \times 6 \times 8)$ $\mathbf{q}$ grid for bulk VTe_2 in 1T phase. The various colors are used to distinguish the number of layers that separate the two atoms in each pair. Vertical lines mark the cutoff radii r_C used to generate the phonon dispersions in fig. 3.13

presented in fig. 3.12, exhibit the same decay behavior, with the aforementioned contribution at a long distance still present, albeit with a slightly lower force constant (2.5×10^{-3} a.u. compared to 5.6×10^{-3} a.u.). This suggests that the contribution is not spurious but rather pertains to the dynamic response of the system.

Furthermore, in this latter plot, it is noticeable that the force constants at longer distances tend to exhibit a slight increase with distance. This phenomenon arises from the fact that at such distances, the impact of a finite supercell becomes significant, causing each atom to be influenced by many periodic images of the others.

To determine an appropriate cutoff radius r_C , various values were tested, with all force constants beyond the selected radius manually set to zero. The phonon dispersion was computed using the `matdyn.x` executable from QE. The results are presented in fig. 3.13 for different cutoff radii, indicated by vertical lines in fig. 3.11 and fig. 3.12, ranging from one lattice constant to the full set of force constants (corresponding to a cutoff radius of $5.1 a$) for the $6 \times 6 \times 4$ $\mathbf{q}$ grid calculation. It is evident from the plot that even with smaller r_C , the system exhibits instability, although the acoustic branches are not accurately reproduced. This implies that such a small cutoff could potentially simulate a

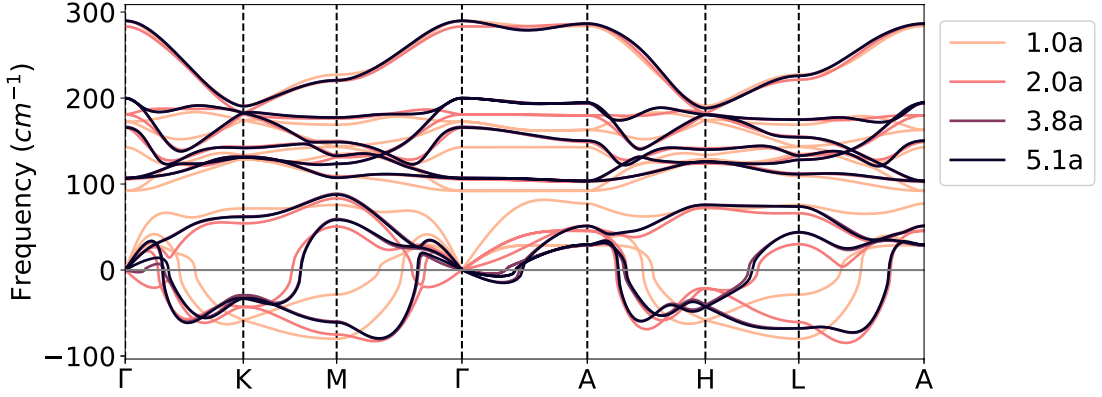


Figure 3.13: Phonon dispersions for bulk VTe_2 in 1T phase computed on a $(6 \times 6 \times 4)$ $\mathbf{q}$ grid and manually setting to zero force constants beyond the cutoff radius r_C . The value of $r_C = 5.1a$ corresponds to the full set of force constants.

phase transition but may not capture the periodicity of the PLD phase and the transition temperature accurately. A cutoff radius of at least $3.8a$ is necessary to achieve an almost perfect agreement with the full set of force constants. Notably, it is crucial to include the aforementioned contribution at a distance of $13.9 \text{ \AA}$ for accurate modeling.

Comparing with the decay of force constants in Figures 3.11 and 3.12, a reasonable criterion for selecting the cutoff radius is to consider the distance beyond which no force constants have values higher than 10^{-3} atomic units. In the case studied thus far, this distance is found to be $3.8a$.

3.3.2 INTERATOMIC POTENTIAL FOR WTe_2

A training set for VTe_2 has not been generated yet and will be the subject of future work. However, our group has already started the development of an IP for another TMD, namely WTe_2 . For this reason approximately 200 uncorrelated configurations from AIMD in its 1T' phase at different temperatures were already available and the preliminary study reported here was performed on this system. In this phase, the WTe_2 monolayer can be described in a rectangular cell with lattice parameters $a = 3.50 \text{ \AA}$ and $b = 6.33 \text{ \AA}$, containing six atoms. MD simulations, constituting the training set, were performed on an almost square (9×5) supercell with a side of approximately $31.5 \text{ \AA}$. This implies a maximum r_C of approximately $15.75 \text{ \AA}$ to account for the PBC. For the unit cell of the WTe_2

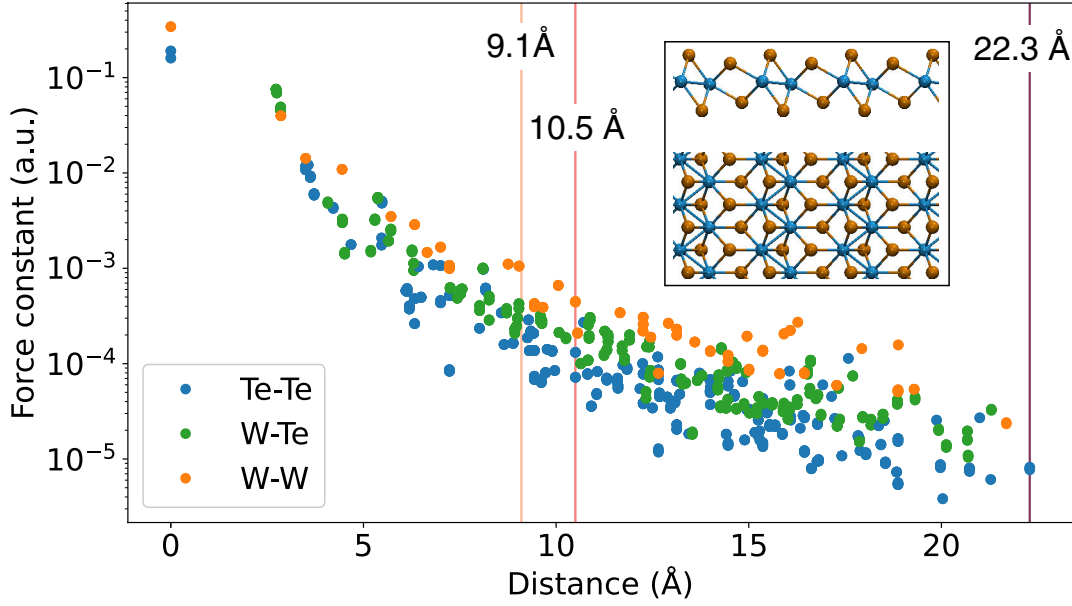


Figure 3.14: Behavior of interatomic force constants as a function of distance between atomic pairs, which were computed on a $(9 \times 5 \times 1)$ $\mathbf{q}$ grid for a monolayer of WTe_2 in $1\text{T}'$ phase. Different colors represent force constants among different atomic species. Vertical lines mark the cutoff radii r_C used to generate the phonon dispersions in fig. 3.15. The inset shows a stick-and-ball model of the system both from a side view (top) and from a top view (bottom).

monolayer, also phonon dispersions and force constants were computed on a $(9 \times 5 \times 1)$ $\mathbf{q}$ grid. The force constants are displayed as a function of distance in fig. 3.14, divided by the types of atoms interacting. They all decay regularly with a power law and just small differences in intensities can be observed between the different atomic species.

Following the reasoning used for VTe_2 , a cutoff radius r_C beyond which the force constants are lower than 10^{-3} atomic units would be chosen. In this case, a value of $r_C = 9.1 \text{ \AA}$ could be selected. Phonon dispersions computed with this cutoff radius are in very good agreement with the full set of force constants (fig. 3.15). However, very small negative frequencies can be observed near the Γ point, still present even using different methods for accounting for the acoustic sum rule. To avoid this issue, a cutoff radius of $r_C = 10.5 \text{ \AA}$ should be considered, which corresponds to taking into account all the force constants higher than 6×10^{-4} atomic units.

Nevertheless, a cutoff radius of $r_C = 9.1 \text{ \AA}$ or even smaller could be a viable choice since the negative contributions are on the order of just 1 cm^{-1} . How-

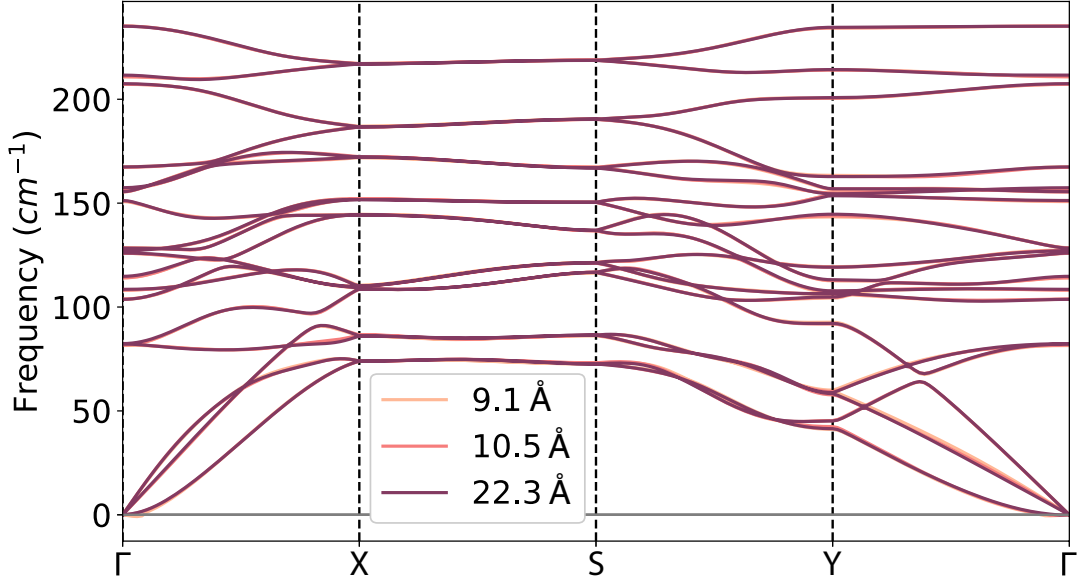


Figure 3.15: Phonon dispersions for a monolayer of WTe_2 in $1\text{T}'$ phase computed on a $(6 \times 6 \times 4)$ $\mathbf{q}$ and manually setting to zero force constants beyond the cutoff radius r_C . The value of $r_C = 22.3 \text{ \AA}$ corresponds to the full set of force constants.

ever, as the dataset has already been generated, and a cutoff of $10.5 \text{ \AA}$ is well beyond half the lattice parameter of the supercell, this value was chosen for the generation of the IP.

The phonon dispersions at 0 K obtained with both the DeePMD and NequIP packages are presented in fig. 3.16 along with the reference DFPT dispersion. Both IPs successfully reproduce all the major features, although NequIP exhibits a better agreement with the reference data, providing a higher accuracy in predicting the absolute values of phonon frequencies. It is important to note that the training set used in this study is relatively small, and no specific tests were conducted to optimize the other hyperparameters of the neural networks. Hence, after further refinement, it is reasonable to expect that the accuracy of the IP will improve.

Therefore, this preliminary study demonstrates the feasibility of using interatomic force constants to determine a cutoff radius for the development of an IP. Indeed, even if phonon calculations are quite computationally demanding, in particular if the number of atoms per cell increases, they are still much less expensive than performing AIMD simulations where due to the high correlation between subsequent frames only one every approximately 100 can be used for constructing the dataset. In particular, in the case of WTe_2 monolayer, this study

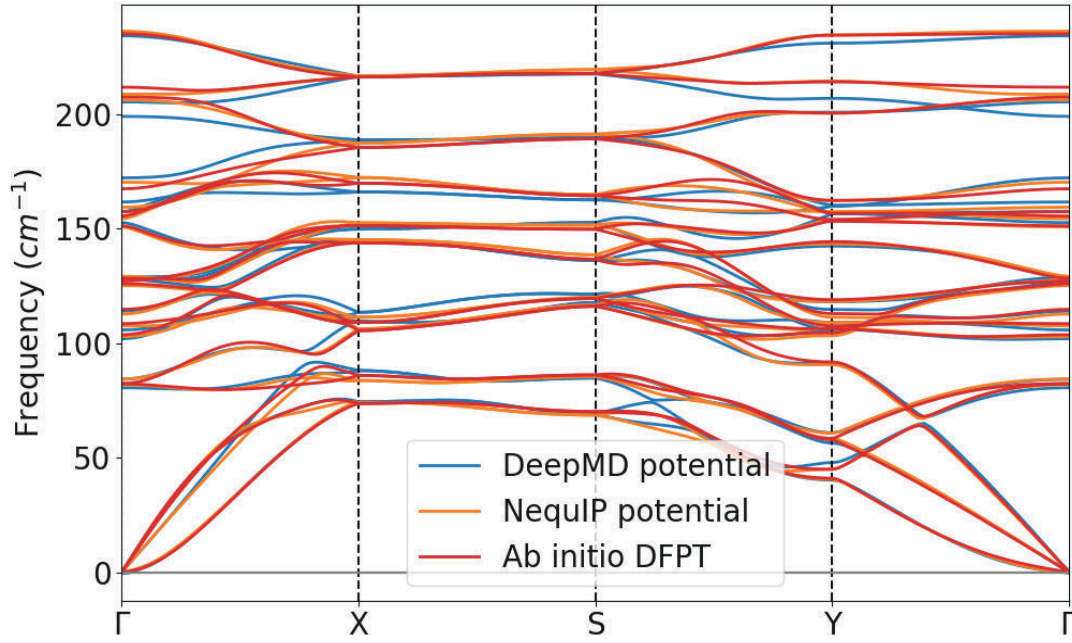


Figure 3.16: Comparison between phonon dispersions for a monolayer of WTe_2 in $1\text{T}'$ phase computed from DFPT and both DeePMD and NequIP machine learning potentials using a cutoff radius of $10.5 \text{ \AA}$.

suggests that a smaller (6×4) instead of a (9×5) supercell could be used in the AIMD simulations hence reducing by nearly 50% the number of atoms to be simulated.

4

Conclusions and outlook

This thesis was primarily dedicated to the computational investigation of two-dimensional and layered materials. The research predominantly relied on first-principles quantum mechanical simulations based on DFT. However, since future investigations would involve the use of machine learning techniques a preliminary study in this direction was also carried on. A crucial aspect of this work was the continuous comparison with experimental findings, which significantly contributed to a comprehensive understanding of the systems under investigation.

The first part of the thesis, presented in the second chapter, focused on the investigation of mono and bimetallic 2D molecular layers based on TPyP. These layers were self-assembled on almost free-standing graphene on Ir(111). The research began with an examination of their geometric structure, highlighting the driving forces behind the self-assembly process. This process was primarily governed by the weak interaction between GR and TPyPs, which ensures high mobility of the molecules on the surface — an essential factor for the formation of long-range ordered structures. Additionally, the precise periodicity and peculiar chiral features of the structure is determined by van der Waals and steric interactions with the substrate and between adjacent molecules. The study also revealed that the introduction of a second metal atom, occupying the intermolecular sites, leads to a significant rearrangement of the molecular layer, resulting in the formation of a 2D metal-organic framework, whose periodicity is highly dependent upon the loading of the additional metallic species.

A detailed characterization of the electronic structure of these layers was

also performed, emphasizing the role of peripheral metal atoms in tuning the electronic properties of the system. Upon bimetallation, the system undergoes a charge transfer, with electrons being donated to the substrate. This results in a rigid shift of approximately 0.7 eV of the electronic states of the porphyrin and a significant reduction in the work function. Furthermore, the study illustrated how the different chemical bonding of Co atoms in the iminic and pyridinic sites led to distinct occupancies of atomic orbitals. Consequently, this led to varying chemical reactivity of the two atoms, with adsorbed CO molecules forming much stronger bonds with peripheral metal species. Interestingly, even the iminic site was found to be chemically active, capable of catalyzing the formation of the OOH molecule and stabilizing it in the presence of water.

The third chapter of this thesis focused on the study of transition-metal dichalcogenides, with a specific focus on bulk VTe_2 in its layered form. By means of DFT techniques both the high-temperature 1T and low-temperature 1T' phases of VTe_2 were investigated. The 1T' phase exhibited periodic lattice distortion, leading to the formation of a charge density wave and significant alterations in the electronic structure of the material, in addition to changes in lattice periodicity compared to the 1T phase. By comparing phonon modes with experimental pump-and-probe experiments, two modes related to the CDW phase were identified with their frequencies exhibiting an experimental damping as the temperature approached the transition temperature.

Furthermore, in anticipation of a more comprehensive examination of this phase transition using MD simulations with interatomic potentials generated through machine learning techniques based on ab initio data, a criterion for establishing a suitable cutoff radius for the interatomic potential was formulated. This was achieved by comparing phonon dispersions computed at different cutoff radii. The results suggested that for the systems under study, a cutoff should take into account all force constants higher than at least 1×10^{-3} atomic units. This criterion was then tested on a WTe_2 monolayer in the 1T' phase for which training data were already available.

The generation of an interatomic potential for VTe_2 , along with a refinement of the one available for WTe_2 , and their use in studying the phase transitions of these transition-metal dichalcogenides, will be the focus of a future work.

5

Appendix

APPENDIX A: DFT CALCULATION DETAILS

This appendix reports the details of the calculations performed in the previous chapters. All DFT calculations were performed with the PBE functional for the exchange correlation terms within the GGA method.

TETRA-PYRIDYL PORPHYRINS AT SURFACES

For all calculations, ultrasoft pseudopotentials were employed. Specifically, Vanderbilt pseudopotentials [8, 104] were used for all atomic species, except for cobalt, for which a pseudopotential from PSLibrary [105] was used. The Hubbard-U correction [106] was introduced to improve the description of the metal atoms' 3d states. A parameter U of 3.5 eV was used for cobalt to reproduce the 5.5 eV energy gap between occupied and unoccupied $3d_{z^2}$ levels, as reported in the literature [107], while a value $U = 6.4$ eV was employed for Fe [57]. Van der Waals interactions were also included using the Grimme-D3 approach [108] because they are essential for obtaining correct molecule-GR and GR-Ir interactions and adsorption energies. Plane-wave cutoffs of 60 Ry and 240 Ry were employed for the wavefunctions and the charge density, respectively. The Methfessel-Paxton smearing scheme was used for the occupation of electronic states, with a smearing parameter of 0.01 Ry [109]. Geometrical optimizations were carried out using the Broyden-Fletcher-Goldfarb-Shanno algorithm, with energy and force convergence thresholds of 1×10^{-6} Ry and 1×10^{-3} Ry/bohr for

the whole cell and for each atomic force component, respectively. The Brillouin zone was sampled using different Monkhorst-Pack grids [6] according to the cell size. In the scf calculations for a single molecule on graphene a $4 \times 4 \times 1$ **k** grid was used, single Γ sampling was used for the simulations with Ir substrate due to the use of large supercell, while a $2 \times 4 \times 1$ **k** grid was employed for both mono and bimetallic systems. Without the Ir substrate also nscf calculations were performed with a double number of **k** points in the in-plane directions.

For CLS and NEXAFS simulations were employed self generated pseudopotentials for N and O species, with a full core hole and half core hole at 1s level.

TRANSITION METAL DICHALCOGENIDES

The results reported in this thesis for both 1T and 1T'' VTe₂ phases were obtained using Pseudo-DOJO norm conserving scalar relativistic pseudopotentials [110] for both V and Te atomic species. Cutoff values of 150 Ry and 450 Ry were employed respectively for the plane wave expansion of wavefunctions and charge density. In order to correctly reproduce the interlayer interactions, van der Waals contributions were explicitly added by means of Grimme-D2 method [111, 112]. In this case the choice of the D2 method resides in the fact that the D3 method is not implemented in `ph.x` code of QE. A Marzari-Vanderbilt-De Vita-Payne smearing scheme [113] with a smearing parameter of 0.01 Ry was applied. For the 1T phase, which has a trigonal Bravais lattice (space group 164, $a = b = 3.597$ Å, $c = 6.699$ Å) a $13 \times 13 \times 6$ **k** grid was used. For the 1T'' phase, which has a monoclinic cell (space group 12, $a = 18.984$ Å, $b = 3.595$ Å, $c = 9.069$ Å, $\beta = 133.3^\circ$) a $12 \times 12 \times 8$ **k** grid was employed.

For VTe₂, ultrasoft pseudopotentials from PSlibrary [105] were also tested using 50 Ry and 400 Ry as cutoffs on wavefunctions and charge density. However, even if for in-plane phonon dispersions the results perfectly aligns with the ones obtained with NCPPs, along **k_z** huge unphysical negative frequencies (~ 2000 cm⁻¹) were predicted.

For the WTe₂ monolayer ultrasoft pseudopotentials from PSlibrary were used. In the unit cell calculations a $26 \times 13 \times 1$ **k** grid was used. Energy cutoffs for the wavefunctions and the charge density were set to 30 Ry and 240 Ry, respectively. A cold smearing with a 0.02 parameter was also employed.

In both VTe₂ and WTe₂ calculations, the convergence parameters were set to 1×10^{-10} Ry for the total energy, 1×10^{-3} Ry/a.u. for the forces and 0.5 kbar

for pressure. A threshold of 1×10^{-14} was set on the self consistency for DFPT calculations.

APPENDIX B: TRAINING DATASET FOR WTe_2 MONOLAYER

A first training dataset for the WTe_2 monolayer was generated by means of Born-Oppenheimer molecular dynamics on a $9 \times 5 \times 1$ supercell computed both in canonical and isobaric ensembles at various temperatures up to 1000 K with a time-step length of 2.42×10^{-3} ps:

Ensamble	Temperature (K)	Lenght (ps)	number of time steps
NVT	200	2.347	970
NVT	300	1.836	759
NVT	500	2.318	958
NPT	1000	1.040	430

Among these, 29 configurations, one every 100, were extracted and randomly divided selecting the 90% for the training and the remaining 10% for the validation sets. In an active learning approach, those data were used for the training of a DeePMD IP employed to perform classical MD at 200, 400, 600, 800 and 1000 K in both NVT and NPT ensembles. Each simulation is 100000 time steps long encompassing 240 ps. One frame every 5000 time steps was extracted and labelled by DFT calculations. The final dataset is composed by 229 frames, 90% of which were used for the training and the remaining 10% for the validation sets.

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